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# THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 61 New Cavendish Street, London, W.1, on 2 April 1958, the Chair being taken by A. C. Hartley, C.B.E., a vice-president of the Institute.

The minutes of the previous meeting were confirmed and signed as a correct record. The names of members elected since the previous meeting were also announced.

The following paper was then presented in summary:

## ANTISTATIC ADDITIVES IN THE PETROLEUM INDUSTRY *

By A. KLINKENBERG † and B. V. POULSTON ‡

SUMMARY

It has been realized for some time that certain operations employed in handling petroleum products can result in the accumulation of electrostatic charges sufficient to cause explosions. These operations include pumping at high speeds through pipelines, settling, etc. The manner in which this charge accumulation can occur is briefly explained.

Experimental work is described in which it is shown that dangerous accumulations of electric charge in oil products can be satisfactorily prevented by increasing the electrical conductivity of the product. This can be achieved by means of an antistatic additive.

In this paper the considerations leading to the discovery of an antistatic additive, of which only a very low concentration need be used, will be outlined. A discussion of its practical possibilities follows, covering points such as: (1) stability of the additive during handling; (2) type of product to be protected by the additive; (3) effect of the additive on specification tests of various products.

### INTRODUCTION

IN spite of the enforcement of strict safety regulations and of the development of handling procedures, which over the years have proved to be safe in the vast majority of cases, disastrous explosions and fires have occasionally occurred with petroleum products. Some of these accidents have obviously been caused by a violation of the safety rules, but in certain cases this possibility has been practically excluded, and it has become more and more likely that the remainder must be largely attributed to a spark discharge caused by an accumulation of static electricity.

The phenomena pertaining to static electricity were, however, insufficiently understood, and it became evident that in order to shed light on certain aspects of the subject, controlled experiments in the laboratory and in full-scale plant were necessary. These have led to the development of a means by which the hazard of static electricity due to flow of hydrocarbon fluids can be reduced to negligible proportions throughout the industry. Neither ignition through lightning nor static electricity generated by steam will be considered in this paper.

### THE GENERATION OF ELECTROSTATIC CHARGE

As a preliminary to the experimental investigation of static electricity, a survey was made covering a considerable number of accidents attributed to this cause over many years. The aspect common to all these cases was that static electricity could have been generated and accumulated in a liquid of very low electrical conductivity. The survey showed that most of these explosions occurred in tanks either during filling or stirring operations or during the settling of water or acid in an oil product.

A further classification of these explosions is shown in Table I.

TABLE I

*Survey of Tank Explosions caused by Liquids in Motion*

| | |
|---|---|
| (*a*) Flow of oil–water or oil–air mixtures in pipelines to storage tanks | 18 |
| (*b*) Stirring up of water bottoms and agitating during treating | 15 |
| (*c*) Splash filling of oil, water, chemical solutions (spent sulphuric acid) into a tank already containing product | 11 |
| (*d*) Settling of treating solutions, or water, out of oil | 2 |

Several accidents in group (*b*) occurred during blending, *e.g.* when a gasoline stream was being introduced just above a water interface, or while introducing butane through a water draw-off line.

It is evident from these data that the generation of static electricity is associated with the movement of liquids relative to one another or to the walls of the pipes in which they flow.

A generally accepted picture of the way in which static electricity is generated by a flowing liquid presupposes the presence in the liquid of ions—positively or negatively charged particles. In hydrocarbons, which themselves cannot produce ions, the ions are

* MS received 14 February 1958.

‡ "Shell" Research Ltd.

† N.V. De Bataafsche Petroleum Maatschappij.

formed by dissociation of small amounts of certain trace substances. Extremely small concentrations of such trace substances will produce sufficient ions to account for the effects observed.

Since, initially, the liquid as a whole is electrically neutral, at least two kinds of ions must be present, carrying charges of opposite signs. These ions will have different affinities for the pipe wall or other material in contact with the hydrocarbon liquids. An excess of ions of one polarity is therefore supposed to form a covering layer over the boundary, while the ions of the other polarity form a mobile second layer in the liquid, very close to the first one. This conception of two layers of oppositely charged ions built up near a boundary of a liquid is known as the "electric double layer," and was first suggested by Helmholtz (1879).

Now, when the liquid is flowing past the boundary the second layer of ions may be stripped from the boundary and be carried away. The liquid will therefore contain an excess of ions of one polarity, *i.e.* it is electrically charged (see Fig 1).

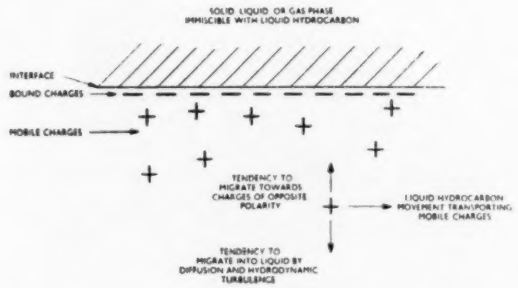
SOLID, LIQUID, OR GAS PHASE IMMISCIBLE WITH LIQUID HYDROCARBON
INTERFACE
BOUND CHARGES
MOBILE CHARGES
TENDENCY TO MIGRATE TOWARDS CHARGES OF OPPOSITE POLARITY
LIQUID HYDROCARBON MOVEMENT TRANSPORTING MOBILE CHARGES
TENDENCY TO MIGRATE INTO LIQUID BY DIFFUSION AND HYDRODYNAMIC TURBULENCE

FIG 1

DIAGRAM ILLUSTRATING THE CONCEPTION OF BOUND AND MOBILE CHARGES, AND THE FEATURES CONTROLLING THE MOVEMENT OF THE MOBILE CHARGES

Of course the charge in the liquid will tend to leak back to the wall by electrical conduction through the liquid, but, provided that the conductivity of the liquid is low enough, the liquid will still contain a charge when it emerges from the pipe.

The electrical conductivity of the liquid is another manifestation of the presence of ions. The fact that oil products do have a certain, though low, conductivity, supports the assumption of the presence of ions on which the picture of charge generation was built.

The specific electrical conductivity of a material is defined as being numerically equal to the conductance of a cube of unit size. For the low conductivities encountered in this work, a convenient unit is 1 picomho/m, which is $10^{-12}$ reciprocal ohm/m (or $10^{-14}$ reciprocal ohm/cm).

The measurement of the conductivity of hydrocarbon products offers some difficulties, largely because of the extremely low concentrations of ions responsible for the conduction. True results can easily be masked by impurities introduced, for instance, during the process of sampling. Too high an electric stress imposed on the liquid in the measuring apparatus can also lead to false readings. This is because in a strong electric field the ions will migrate rapidly to the electrodes.

The following is a standard method, employed by various teams studying the electrification of petroleum

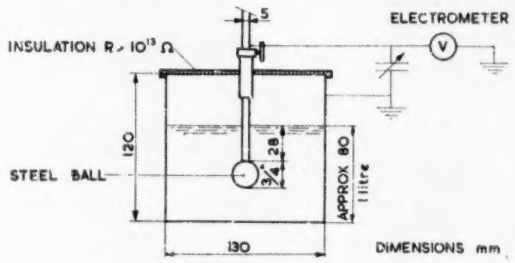


FIG 2

APPARATUS FOR DETERMINATION OF CONDUCTIVITY

products. A condenser of standard size is formed, using a sample of the hydrocarbon liquid as the dielectric. As shown in Fig 2, one electrode consists of a sphere suspended in the liquid at the centre of a container and the other electrode is formed by the container. A small known voltage is applied to the central electrode, and the time taken for this voltage to decrease to a standard fraction of its initial value is measured. From knowledge of the capacitances in the system and the dielectric constant of the liquid the conductivity of the sample is then calculated.

TABLE II

*Conductivities of some Petroleum Products*

| Product | Conductivity, picomho/m |
|---|---|
| White spirit | 0·02– 1 |
| Motor gasoline | 0·3 – 10 |
| Kerosine | 0·02– 40 |
| Gas oil | 600 – 1200 |
| Crude oils | 1500 –70,000 |

In order to obtain reliable results with this apparatus, scrupulous cleanliness should be observed and standardization procedures should be carried out frequently.

It is significant that in all accidents ascribed to static electricity white products have been involved. These not only include the products which most readily form inflammable vapour–air mixtures, but from Table II it will also be seen that white products have the lowest conductivities.

Potentially the most dangerous products are those having conductivities below 10 picomho/m. There is a certain level of conductivity above which oil products can be safely handled. The reasons for this will be explained in the following section, where the conditions inside the tank receiving the charged product will be considered.

## THE REQUIRED LEVEL OF CONDUCTIVITY

During the filling of a tank, a balance is reached between the rate of generation of electricity, caused by the flow of oil through the pipeline, and the rate of dissipation of electricity after the charged oil has reached the tank. For a given rate of generation of electricity the amount of charge present at any moment in the tank will be small if the charge is easily dissipated or, in other words, if the specific conductivity of the oil product is high. Conversely, if the conductivity is low, a much larger amount of electricity will accumulate in the contents of the tank.

If an earthed metal tank is wholly filled with a charged oil product, and if there is no further charge being added to the product, the time needed to reduce the value of the electric charge to half its original value is inversely proportional to the conductivity and proportional to the dielectric constant of the liquid. This time is known as the half-value time.*

For most hydrocarbons the dielectric constant is about 2, and for this value the relationship between conductivity and half-value time is shown in Fig 3.

The question now arises as to what level of conductivity is necessary to render the handling of oil products safe. First, however, a criterion of safety must be defined. The fundamental criterion is, of course, that there should be no spark, and this implies that a certain critical electric field strength should not be exceeded.

It is, however, not possible to predict beforehand exactly when and where this critical field strength will be exceeded, except for some very simple cases. Therefore an empirical approach is required.

It should be realized that the field strength distribution in an actual tank is very complicated because of the influence of the tank structure and other internal fittings. It has thus been the practice to measure the vertical component of the field strength in the centre of the tank, above the liquid level. The assumption is then made that the highest electric field strength, wherever it may occur inside the tank, is proportional to the value measured.

Very strong fields were recorded in this way while product was being pumped into a tank, and these fields were particularly strong when two phases (*e.g.* oil–water) were being pumped together. Field strengths of up to 100 kV/m were observed quite regularly in a large tank, in which a field meter was suspended several metres above the surface of the liquid.[1] In another, smaller tank, 590 kV/m has been measured in an explosive atmosphere, and even at this considerable field strength no ignition occurred.

As mentioned above, these high field strengths were measured in the top of the tank, and even higher field strengths must have existed locally, owing to the tank structure. The surface of the oil in the tanks must have occasionally reached potentials as high as half a million volts without an explosion occurring.

In view of the difficulty of obtaining precise information as to what field strength constitutes a dangerous situation, it was assumed that a sufficient margin of safety would be established if the values of field strength normally caused by an operation were reduced to a very small fraction.

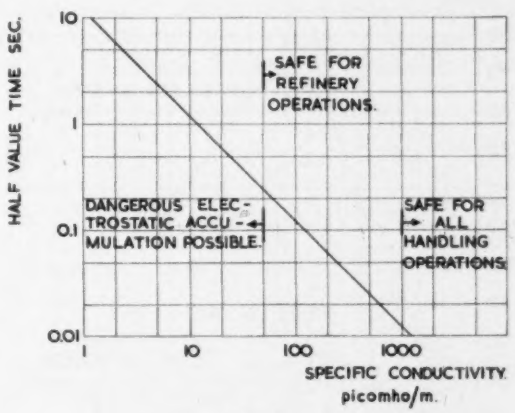


FIG 3

RELATIONSHIP BETWEEN SPECIFIC CONDUCTIVITY AND HALF-VALUE TIME, FOR HYDROCARBONS ($\varepsilon = 2$)

In the same investigation the principle was demonstrated that by increasing the conductivity of the oil product, the field strength could be reduced by the required amount.

A large-scale research programme has been carried out for the purpose of deciding upon the level of conductivity above which the hazard due to static electricity can be considered negligible. In the course of these experiments particular attention has been given to the effect of the type of operation and of certain contaminants and additives.

Care is necessary in interpreting the effectiveness of additives. Even if the conductivity imparted by different additives is the same, the charge generated may still be different, the degree of charging depending on the nature of the wall and its affinity for the ions.

This has been confirmed by experiments in which

* The relaxation time is another concept which is frequently mentioned in theoretical discussions on static electricity. It is the half-value time divided by ln 2.

the charging properties of "Cr–AC" additive * and of the corrosion inhibitor Nasul EDS have been studied. These have been compared in steel pipes and in two types of filter, with various concentrations of additive. Usually the corrosion inhibitor charged more strongly, but sometimes the Cr–AC was more active in this respect, at corresponding conductivities (Fig 4).

In order to obtain reproducible results in the large-scale experiments, these have been carried out with relatively pure hydrocarbons, containing known amounts of certain electrically active compounds. It has become clear that the charging activity of these compounds was comparable with that of the naturally occurring substances (oxidation products, asphaltenes) causing the electric effects.

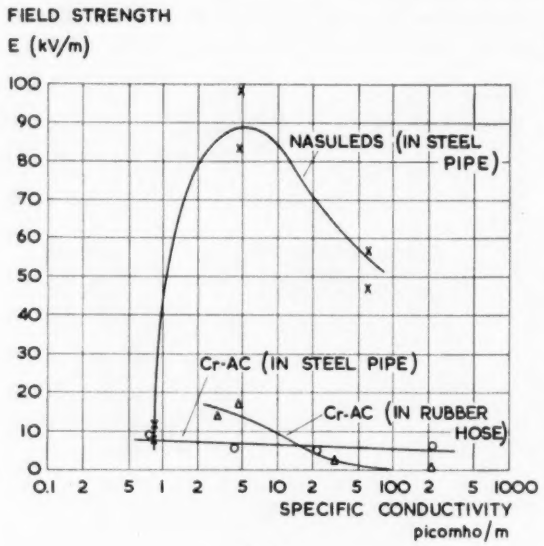


FIG 4

A COMPARISON OF THE ELECTRIC FIELD STRENGTH CAUSED BY DIFFERENT ADDITIVES

The liquid is kerosine, flowing at approx 9 m/sec.

The refinery operations studied were the pumping of oil into refinery tanks, either with or without the addition of water to the oil, and the mixing of oil products in such tanks. Other experimental work covered the pumping of kerosine into a small tank, at high rates of flow, through a 2-inch diameter rubber hose or steel pipe. Work was also done on the electrostatic charging effect of filters. In each series of experiments both the linear velocity of flow and the conductivity were varied.

The results showed that in refinery operations virgin products, which usually have conductivities less than 5 picomho/m, can produce very strong electric fields. However, if the conductivity was increased by means of antistatic additive to a value between 20 and 50 picomho/m the electric field strength was reduced very considerably. Above 50 picomho/m the situation was considered safe, even under very adverse circumstances, *e.g.* when pumping oil–water mixtures. In the high-speed pumping test rig it was shown that high flow rates in rubber hoses and in steel pipes up to 10 m/sec may cause such intensive generation of electricity that a conductivity of 500 picomho/m is needed in order to reduce the electric effect sufficiently. It was found that the same value was also adequate to deal with electrification caused by filters.

In view of these and other tests, it can be stated that oil products which have a conductivity of the order of 1000 picomho/m may be considered safe, not only during normal refinery handling and operations, but also in situations where extreme electrification occurs (see also Klinkenberg [2]).

## THE EFFECT OF ADDITIVES ON CONDUCTIVITY

In the preceding section the conclusion was reached that in order to safeguard operations the conductivity of oil products should, in principle, be raised to a value of about 1000 picomho/m. This value allows a comfortable safety margin. In fact, for normal handling and refinery operations the safety margin may well be considered unduly large, since in these cases it amounts to a factor of about 20. The problem now is to determine what additives can be used to reach this desired conductivity and what, if any, are their side effects.

TABLE III

*The Concentration of Various Additives Required to Reach a Conductivity of 1000 picomho/m in Hydrocarbons*

| Solvent | Solute | Concn, kmol/m³ | Mol. wt, kg/kmol | Concn, kg/1000 m³ | Source of data |
|---|---|---|---|---|---|
| Benzene | Asphaltenes | — | — | 17 | (1) p. 78 |
| Dry cleaners' Naphtha | Ethanol | 1·75 | 46 | 80,000 | (3) interpolated |
| | Mg oleate | $5 \cdot 10^{-4}$ | 586 | 293 | |
| Benzene | Tiap [1] | $10^{-4}$ | 526 | 53 | (1) p. 79 |
| " | CaDips [2] | $5 \cdot 10^{-3}$ | 482 | 2400 | (1) p. 79 |
| Gasoline | Ca aerosol OT [3] | $10^{-3}$ | 2000 | 2000 | (1) p. 83 |
| " | Cr–AC [4] | $2{,}5 \cdot 10^{-3}$ | 2500 | 6·2 | (1) p. 83 |
| Gasoline | Shell antistatic additive [5] | — | — | 2 | (1) p. 83 |

[1] Tiap = tetra-*iso*amyl ammonium picrate.
[2] CaDips = calcium di-*iso*propyl salicylate.
[3] Solution of the calcium salt of di(2-ethylhexyl)sulphosuccinic acid, containing 2·0 wt % Ca, 55 wt % inert solvent, apparent mol. wt. = 2000.
[4] Solution of the chromium salt of a mixture of mono- and di-alkyl salicylic acid, the alkyl chains of which contain 14–18 carbon atoms, containing 2·1 wt % Cr, 30 wt % inert solvent, apparent mol. wt. = 2500.
[5] Mixture of equal amounts of the solutions of Ca Aerosol OT and Cr–AC containing 42 wt % of inert solvent, 1·0 wt % Ca, 1·05 wt % Cr.

In Table III, data have been collected on the concentration of various additives required to raise the

* Cr–AC is a solution of the chromium salt of a mixture of mono- and dialkyl salicylic acid, the alkyl chains of which contain 14–18 carbon atoms.

conductivity of a light hydrocarbon to 1000 picomho/m.

Several polar organic substances (alcohols, amines, mercaptans, acids, esters) have been examined by Hampel and Luther,[3,4] but only with a large amount of ethanol could the figure of 1000 picomho/m be reached. The further data in Table III refer to asphaltenes (which might also be added in the form of asphalt or crude oil), various metal salts, and a salt of an organic base.

In order to reduce any side effects to a minimum it is essential to use the smallest possible amount of additive. This can be achieved by employing a principle described by van der Minne and Hermanie.[1,5] Briefly stated, this principle says that certain combinations of substances, suitably chosen, will impart a conductivity which is far higher than the sum of the conductivities produced by each of the substances alone. Two most effective substances are the Cr–AC and the Ca–AEROSOL OT referred to in Table III. The best combination consists of nearly equimolar amounts of these constituents. The activity of this combination compares very favourably with that of other additives, as shown in Table III.

A concentrated solution of this optimum combination of additives has been prepared, and this will be referred to as "Shell antistatic additive." This solution contains 1·05 per cent of chromium and 1·0 per cent of calcium. The recommended dosage is 2 kg/1000 m³ (0·7 lb/1000 brl) of product. This is sufficient to achieve a safe level of conductivity. The effect of different concentrations of Shell antistatic additive on the conductivity of a gasoline is shown in Fig 5.

Products which are not filtered or pumped at high speeds could in principle be doped to a much lower level. However, at such a low level the loss of additive, due to adsorption, leaching, etc., would be more probable and might be difficult to control.

As it is also much simpler to use the same dosage for all products and as the cost of the additive is hardly a factor in its application, the same dosage is proposed whatever the product. It should be realized, though, that in some products the conductivity imparted by the antistatic additive, at this concentration, may well differ from 1000 picomho/m because factors like viscosity and aromaticity may considerably affect its activity. The conductivity realized by the proposed dosage will, however, always allow a considerable margin of safety.

It should be pointed out that adjusting the conductivity of the fuel by means of antistatic additive provides full protection in those cases only where the low conductivity of the fuel is the deciding factor in the accumulation of static electricity. However, when there is a large resistance not due to the hydrocarbon, *e.g.* when pumping hydrocarbons into an insulated container, there is always a dangerous situation, since a spark may pass from the container to earth. The bonding of all equipment remains therefore mandatory. It must also be remembered that the antistatic additive will not afford protection against charging caused by processes other than the movement of the product, *e.g.* by steam jets.

## STABILITY OF THE ANTISTATIC ADDITIVE

The first requirement of any additive is that it should not decompose during storage. Shell antistatic additive was found to be quite stable in this respect, both in glass and in iron containers. Samples have been stored for over a year without showing any sign of chemical instability. For the purpose of incorporating the additive in the refinery it has, at one place, been the practice to prepare an intermediate solution containing 0·4 kg/m³. This solution has

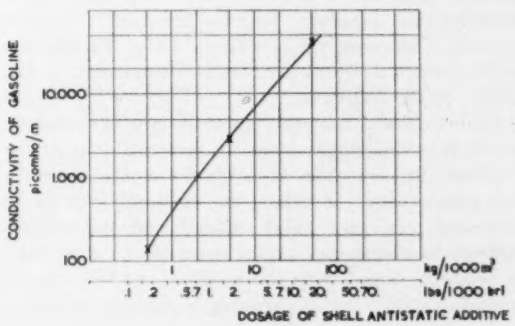


FIG 5

CONDUCTIVITY IMPARTED BY SHELL ANTISTATIC ADDITIVE TO A GASOLINE

(Boiling range 80°–110° C)

also been in storage for a considerable length of time without showing any deterioration.

It is also very important that the additive is not removed from the product by any physical process to which the product may be subjected in the course of normal handling. Any such removal might well cause a serious depletion of the additive, since the dosages employed are themselves extremely small. In fact, one of the main difficulties overcome during the development of the additive was to ensure its stability in the presence of water, which is often present as a separate phase in oil products at some stage in their life. It was found that one of the components considered during earlier stages of the development tended to be leached out by water. It was replaced by Cr–AC and no further trouble was encountered.

It was expected that the additive might also be depleted by excessive adsorption on the surfaces with which the product was in contact, *e.g.* pipe walls and filter beds. However, no serious depletion was

encountered over an extended period of study, with the sole exception of passage through a new unimpregnated paper filter. This persisted only until the filter surface and the product had reached equilibrium.

In order to establish the suitability of the additive for the protection of tanker loading and subsequent handling operations, a number of trial shipments were made. For these experiments an intermediate product in the heavy naphtha range was chosen. This product is regularly being shipped across the Channel, and, since the vapour above the liquid is in the explosive range, these shipments constituted the first practical application of the dope for the protection of dangerous products.

The concentration of the additive in the product was determined in the storage tanks before the loading of the tanker and checked on arrival at the point of destination, after the discharge of the tanker. The concentrations of additive are so small that the normal analytical methods are not sufficiently sensitive to measure them. The only feasible method of assessing the concentration of the additive in a product is by measuring the conductivity imparted by the additive.

Unfortunately, however, the activity of the additive is not only dependent upon its concentration in the product but also upon such factors as the viscosity and aromaticity. Further, the conductivities to be measured are very small indeed and accordingly difficult to determine. Data collected for a number of products doped with the additive can thus be expected to show a certain amount of random variation.

TABLE IV

*Conductivity of a heavy naphtha, doped with 2 kg/1000 m³ of additive, before and after shipment*

| Before loading, picomho/m | After discharge, picomho/m |
|---|---|
| 1100 | 1200 |
| 5000 | 1300 |
| 2300 | 600 |
| 2000 | 350 |
| 1300 | 700 |
| 2800 | 1750 |
| 1000 | 700 |
| Average 2200 | 950 |

During these experiments it was also discovered that there is an ageing effect. A freshly doped product has a conductivity which may be twice as high as the value found later for the same product. The major part of this drop in conductivity occurs within 24 hours of the doping, and after one or two weeks the conductivity remains approximately constant.

In the light of the above it will be seen from Table IV that the behaviour of the antistatic additive during shipment may be considered satisfactory. On the average the fuel arrives with a conductivity of the order of 1000 picomho/m, which is the desired value. In no case has the conductivity been reduced to below the value of 50 picomho/m considered safe for refinery handling. The experiments are still in progress, and improved testing methods are being developed.

## TYPES OF PRODUCT TO WHICH ANTISTATIC ADDITIVE SHOULD BE APPLIED

It is required to protect the refinery and the subsequent distribution system wherever a volatile product is involved, of which the vapour forms an inflammable mixture in the air space above the liquid.

Under equilibrium conditions, mixtures of air and hydrocarbon vapours are inflammable only when the concentration of hydrocarbon vapour lies between certain limits, known as the " weak limit " and the " rich limit."

The concentration achieved in any given case will depend on the ambient temperature, and as an approximate guide Fig 6 has been prepared.

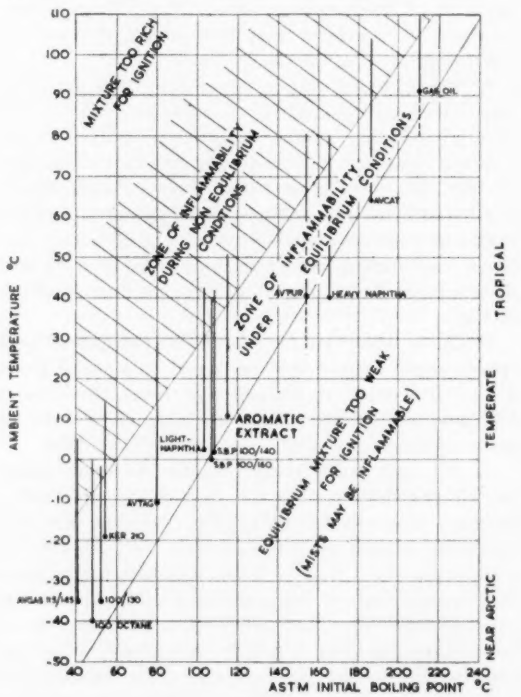


FIG 6

THE INFLAMMABILITY OF THE VAPOURS ABOVE VOLATILE HYDROCARBONS (CHARACTERIZED BY THE ASTM I.B.P.) AS A FUNCTION OF THE AMBIENT TEMPERATURE

This figure shows the range of ambient temperature over which certain products form inflammable air–vapour mixtures. The products are characterized somewhat arbitrarily by their ASTM Initial Boiling Points, but it is, of course, equally possible to prepare

TABLE V

*The Effect of Antistatic Additive on Specification Properties of AVTAG*

| Tests | Specification D.Eng.R.D. 2486 | AVTAG—Source A | | AVTAG—Source B | |
|---|---|---|---|---|---|
| | | Without additive | With 6 p.p.m. additive | Without additive | With 6 p.p.m. additive |
| Appearance | Clear, no water, sediment or suspended matter | Pass | Pass | Pass | Pass |
| Colour | — | Colourless | Colourless | Colourless | Colourless |
| Acidity, total, mg KOH/g | 0·10 (max) | <0·05 | <0·05 | <0·05 | <0·05 |
| Aromatics, % vol | 25 (max) | 14 | 14 | 13 | 13 |
| Olefins, % vol | 5 (max) | <1 | <1 | <1 | <1 |
| Corrosion (copper strip) | No corrosion, not more than slight tarnish | Pass (ASTM 1a) | Pass (ASTM 1a) | Pass (ASTM 1a) | Pass (ASTM 1a) |
| *Distillation:* | | | | | |
| % evap. at 143° C | 20 (min) | 49·5 | 50·5 | 48·5 | 49 |
| % evap. at 188° C | 50 (min) | 89 | 89 | 86 | 86 |
| % evap. at 204° C | — | 94·5 | 94·5 | 90·5 | 91 |
| % evap. at 243° C | 90 (min) | — | — | — | — |
| F.B.P., ° C | — | 226 | 227 | 242 | 242 |
| Residue, % vol | 1·5 (max) | 1·0 | 1·0 | 1·0 | 1·0 |
| Loss, % vol | 1·5 (max) | 0·5 | 0·5 | 0·5 | 1·0 |
| Freezing point, ° C | −60 (max) | <−60 | <−60 | <−60 | <−60 |
| Existent gum, mg/100 ml | 7 (max) | < 1 | < 1 | < 1 | < 1 |
| Accelerated gum, mg/100 ml | 14 (max) | 1 | 1 | 1 | 1 |
| Aniline gravity product | 5250 (min) | 7400 | 7400 | 7500 | 7450 |
| S.V.I. | 54 (min) | 70 | 71 | 67 | 67 |
| Specific gravity, 60/60° F | 0·751–0·802 | 0·757 | 0·758 | 0·7575 | 0·7585 |
| Sulphur, mercaptan, % wt | 0·005 (max) or Doctor sweet | Doctor sweet | Doctor sweet | Doctor sweet | Doctor sweet |
| Sulphur, total, % wt | 0·4 (max) | 0·09 | 0·09 | 0·08 | 0·08 |
| *Water reaction:* | | | | | |
| Volume change, ml | 1·0 (max) | Nil | Nil | Nil | Nil |
| Separation | Sharp separation, no emulsion precipitate or suspended matter | Pass | Pass | Pass | Pass |
| Interface rating | 1b (max) | 1 | 1 | 1 | 1 |

TABLE VI

*The Effect of Antistatic Additive on Specification Properties of Aviation Gasoline*

| Tests | Specification D.Eng.R.D. 2485 | 100/130 AVGAS | | 115/145 AVGAS | |
|---|---|---|---|---|---|
| | | Without additive | With 6 p.p.m. additive | Without additive | With 6 p.p.m. additive |
| Specific gravity 60/60° F | — | 0·7215 | 0·723 | 0·708 | 0·709 |
| Suspended matter sediment and water | Nil | Nil | Nil | Nil | Nil |
| Colour | Green | Green | Green | — | — |
| | Purple | — | — | Purple | Purple |
| Aniline gravity product | 7500 (min) | 8450 | 8400 | — | — |
| | 9000 (min) | — | — | 10,300 | 10,200 |
| Weak mixture rating: | | | | | |
| AN-P No. (IP 150) ex F2 | 99 ON (min) | 101·2 AN-PN | 101·2 AN-PN | — | — |
| AN-P No. (IP 42) F3 | 115 AN-PN (min) | — | — | 117·7 | 117·7 |
| *Distillation:* | | | | | |
| 10% + 50% evap. temp, ° C | 135 (min) | 160 | 160·5 | 162 | 163·5 |
| Final boiling point, ° C | 170 (max) | 162 | 163 | 163 | 164 |
| Dist. residue, % vol | 1·5 (max) | 1·0 | 1·0 | 1·0 | 1·0 |
| Dist. loss, % vol | 1·5 (max) | 1·0 | 1·0 | 1·0 | 1·0 |
| Evap. at 75° C, % vol | Between 10 and 40 | 18·5 | 18·5 | 23·5 | 21·5 |
| Evap. at 105° C, % vol | 50 (min) | 70 | 70 | 57 | 55·5 |
| Evap. at 135° C, % vol | 90 (min) | 90 | 90 | 92·5 | 92·5 |
| Vapour pressure (Reid) at 100° F, p.s.i. | 5·5–7·0 | 5·85 | 5·20 | 5·90 | 5·45 |
| Existent gum, mg/100 ml | 3·0 (max) | 3 | 3 | 3 | 3 |
| Accelerated gum, mg/100 ml | 6·0 (max) | 5 | 5 | 3 | 3 |
| Freezing point, ° C | −60 (max) | <−60 | <−60 | <−60 | <−60 |
| Total sulphur, % wt | 0·05 (max) | 0·03 | 0·03 | 0·03 | 0·03 |
| Corrosion (copper strip) | Slight discoloration (max) | Passes (ASTM 1a) | Passes (ASTM 1a) | Passes (ASTM 1a) | Passes (ASTM 1a) |
| *Water Reaction:* | | | | | |
| Emulsion precipitate or suspended matter within or upon either layer | Nil | Nil | Nil | Nil | Nil |
| Change in volume | 2 (max) | Nil | Nil | Nil | Nil |
| Interface rating | 2 (max) | 1 | 1 | 1 | 1 |

TABLE VII

*The Effect of Antistatic Additive on Specification Properties of AVTUR*

| Tests | Specification D.Eng.R.D. 2482 | AVTUR—Source A | | AVTUR—Source B | |
|---|---|---|---|---|---|
| | | Without additive | With 6 p.p.m. additive | Without additive | With 6 p.p.m. additive |
| Suspended matter and deposit | Nil | Nil | Nil | Nil | Nil |
| Specific gravity, 60/60° F | 0·775–0·825 | 0·799 | 0·799 | 0·7915 | 0·7915 |
| Gravity, °API | 51–40 | 45·6 | 45·6 | 47·3 | 47·3 |
| Colour (Lovibond 18-inch cell) | 4·0 (max) | 0·5 | 0·5 | 0·5 | 0·5 |
| Kinematic viscosity at 0° F, cS | 6·0 (max) | 3·95 | 3·93 | 3·29 | 3·27 |
| *Distillation:* | | | | | |
| I.B.P., °C | — | 154 | 155 | 153 | 153 |
| 20% vol rec. at °C | — | 180 | 180 | 170·5 | 171 |
| 50% vol rec. at °C | — | 200 | 200 | 188 | 188 |
| 90% vol rec. at °C | — | 234 | 233·5 | 226·5 | 227 |
| F.B.P., °C | 300 (max) | 252 | 251 | 248 | 248 |
| Recovery at 200° C, % vol | 20 (min) | 50 | 50 | 66 | 65 |
| Residue, % vol | 2·0 (max) | 1·0 | 1·0 | 1·0 | 1·0 |
| Loss, % vol | 1·5 (max) | 0·5 | 0·5 | 0·5 | 0·5 |
| Flash point, °F | 100 (min) | 107 | 107 | 102 | 101 |
| Freeze point, °F | −40 (max) | −63 | −63 | −76 | −76 |
| Total sulphur, % wt | 0·20 (max) | 0·10 | 0·09 | 0·09 | 0·10 |
| Mercaptan sulphur, % wt | 0·005 (max) | Doctor sweet | Doctor sweet | Doctor sweet | Doctor sweet |
| Corrosion (copper strip) | Slight discoloration (max) (ASTM 1b) | Pass (ASTM 1a) | Pass (ASTM 1a) | Pass (ASTM 1a) | Pass (ASTM 1a) |
| Existent gum, mg/100 ml | 3·0 (max) | <1 | <1 | <1 | 1 |
| Accelerated gum, mg/100 mg | 6·0 (max) | <1 | <1 | <1 | 1 |
| Aromatic content, % vol | 20 (max) | 16 | 16 | 15 | 15 |
| Olefin content, % vol | 5 (max) | 1 | 1 | 1 | 1 |
| Inorganic acidity | Nil | Nil | Nil | Nil | Nil |
| Aniline gravity product | 4500 (min) | 6500 | 6500 | 6650 | 6650 |
| *Water reaction:* | | | | | |
| Volume change, ml | 1 (max) | Nil | Nil | Nil | Nil |
| Separation | Sharp separation, no emulsion precipitate or suspended matter | Pass | Pass | Pass | Pass |
| Interface rating | 1b (max) | 1 | 1 | 1 | 1 |
| Pour point, °F | — | −65 | −70 | −80 | −80 |

a similar plot based on another product property, such as Reid vapour pressure, flash point, etc.

It must be emphasized that the above information refers only to equilibrium conditions, which, although rapidly established at the surface of the liquid, may take many hours or days to become established in the upper regions of the tank. Dangerous mixtures can occur in the interim period.

With a tank already containing a product, it is likely that the vapour space will be occupied by a vapour–air mixture approximating to the equilibrium conditions. Fig 6 then applies during the subsequent filling or mixing process, and if the ambient temperature lies between the limits shown for the product an inflammable mixture will be present.

With a tank initially empty and clean, on the other hand, no hydrocarbon vapour will be present when filling begins. From this stage onwards, evaporation takes place so that the mixture composition in the space above the liquid approaches the equilibrium value for the particular ambient temperature. If this temperature is above the " rich limit " it follows that, at some time during the filling process, the composition in part or in the whole of the space will pass through the " weak limit " into the zone where it will be inflammable. Only after some time will the composition of the mixture pass the " rich limit " into the non-inflammable zone.

An ill-defined extension must thus be added above the lines shown on Fig 6 to denote a zone in which inflammable mixtures will exist during the time that equilibrium conditions are being established in the tank ullage, *i.e.* during filling or during the mixing of products of different volatilities. This applies, for instance, in the case of empty tanks which have been cleaned between cargoes in order to avoid contamination. Therefore, products such as gasoline, which normally have over-rich air–vapour mixtures, should also be protected.

During many operations it is possible for some of the products to be physically broken up to form spray or mist above the liquid. In this event an inflammable mixture of mist and air can be obtained in conditions where the equilibrium vapour–air mixture is too weak to burn. Therefore, below the lines of Fig 6 there is a region where there may be an inflammable mist.

From Fig 6 as shown, it must be concluded that

inflammable mixtures can occur in temperate climates with products ranging from gasoline via naphthas to kerosine. It is all the more necessary to include gasoline and kerosine in the group of dangerous products if near-Arctic and tropical conditions are also to be taken into account.

Thus, in order to reduce everywhere the risk of explosions caused by static electricity, it is desirable to include the antistatic additive in all white products.

Explosive mixtures might also occur in tanks containing untopped crudes. In this case, protection against build-up of static charges during pumping is inherent in the product, since its conductivity, as mentioned in a previous section, is naturally high.

## SUITABILITY OF ADDITIVE IN RESPECT OF PRODUCT QUALITY

Work is proceeding on the intricate task of checking that the additive in no way affects the quality of the product into which it is blended, and that the conductivity-increasing properties of the additive are not seriously impaired by the presence of other additives. Results are sufficiently encouraging for a brief account to be presented.

The product of most concern from the point of view of inflammability is the wide range aviation turbine fuel (AVTAG or JP–4 type), large quantities of which are being handled in the refinery and throughout the distribution system. Moreover, in the course of its further handling it is subjected to filtration and high-speed pumping. Effort has therefore been directed first and foremost towards studying the suitability of the additive in this product and its components.

The results of testing the specification properties of samples of AVTAG (or JP–4 type) drawn from different sources are given in Table V. Samples were dosed with additive to an extent far greater than that necessary to obtain protection from electrostatic charging. For comparison, results of tests on samples of the fuels without additive are included.

Clearly the Shell antistatic additive does not alter the specification properties of this fuel even in such an excessive concentration.

As described in the previous section, other types of aviation fuels can in certain circumstances become inflammable during handling. The effect of the additive on product quality has also been checked for these products, and the results are shown in Tables VI, VII, and VIII for aviation gasoline, aviation kerosine (AVTUR or JP–1 type), and high flash kerosine (AVCAT or JP–5 type) respectively.

TABLE VIII

*The Effect of Antistatic Additive on Specification Properties of AVCAT*

| Tests | Specification D.Eng.R.D. 2488 | AVCAT | |
|---|---|---|---|
| | | Without additive | With 6 p.p.m. additive |
| Suspended matter and deposit | Nil | Nil | Nil |
| Colour | — | Colourless | Colourless |
| Specific gravity at 60/60° F | 0·788–0·845 | 0·821 | 0·821 |
| Gravity, ° API | 48–36 | 40·8 | 40·8 |
| Kinematic viscosity at −30° F, cS | 16·5 (max) | 10·8 | 10·9 |
| *Distillation:* | | | |
| I.B.P., ° C | — | 186 | 187 |
| 20% v rec. at ° C | — | 203 | 203 |
| 50% v rec. at ° C | — | 215 | 215 |
| 90% v rec. at ° C | — | 241 | 241 |
| F.B.P., ° C | 288 (max) | 258 | 258 |
| Residue, % vol | 1·5 (max) | 1·0 | 1·0 |
| Loss, % vol | 1·5 (max) | 1·0 | 1·0 |
| % v evap. at 204° C | 10 (min) | 23·5 | 23·5 |
| Flash point, ° F | 140 (min) | 148 | 146 |
| Freeze point, ° F | −40 (max) | −53 | −49 |
| Total sulphur, % wt | 0·4 (max) | 0·11 | 0·11 |
| Mercaptan sulphur, % wt | 0·005 (max) | 0·001 | 0·001 |
| Corrosion (copper strip) | Slight discoloration (ASTM 1b) (max) | Pass (ASTM 1a) | Pass (ASTM 1a) |
| Existent gum, mg/100 ml | 7·0 (max) | <1 | <1 |
| Accelerated gum, mg/100 ml | 14·0 (max) | <1 | 1 |
| Aromatic content, % vol | 25 (max) | 21 | 21 |
| Olefin content, % vol | 5 (max) | 1 | 1 |
| Total acidity, mg KOH/g | 0·10 (max) | 0·05 | 0·05 |
| Aniline gravity product | 4500 (min) | 5550 | 5550 |
| Smoke point, mm | 18 (min) | 19 | 19 |
| *Water reaction:* | | | |
| Volume change, ml | 1 (max) | Nil | Nil |
| Separator | Sharp separation, no emulsion precipitate or suspended matter | Pass | Pass |
| Interface rating | 1b (max) | 1 | 1 |

TABLE IX

*The Effect of Antistatic Additive on Properties of Illuminating Kerosine*

| Test | Kerosine A | | Kerosine B | | Kerosine C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Without additive | With 3 p.p.m. antistatic additive | Without additive | With 3 p.p.m. antistatic additive | Without additive | With Chromium AC in concentration | | | | With 6 p.p.m. antistatic additive |
| | | | | | | 0·1 p.p.m. | 0·3 p.p.m. | 1 p.p.m. | 3 p.p.m. | |
| Smoke point (IP 57), mm | 42 | 42 | 34 | 34 | 24 | 24 | 24 | 24 | 24 | 24 |
| 24 hr burning test (IP 10): | | | | | | | | | | |
| Wt. dry char, mg/kg oil burned | 2 | 2 | 13 | 13 | 18 | 18 | 19 | 19 | 20 | 20 |
| Condition of glass— | | | | | | | | | | |
| (1) Colour | Blue/brown | Blue/brown | Blue/brown | Blue/brown | Light grey | | Light grey | | | Grey/brown |
| (2) Remarks | Normal | Normal | Normal | Normal | | | | | | |

The additive was incorporated in a concentration of 3 kg/1000 $m^3$, which is probably more than will be required for protection. No adverse effects were detected at this concentration.

As part of the study of the high temperature stability of aviation turbine fuels and the use of the CFR Fuel Coking Rig to assess this characteristic, the effect of the additive on thermal stability is under investigation. Results are encouraging, and suggest that the additive does not affect thermal stability under 300°–400° F conditions in AVTAG or JP–4 type fuels, and under 400°–500° F conditions in AVCAT or JP–5 type fuels.

One of the tests which is most likely to be affected by small doses of any additive is the IP 10 burning test. Table IX shows the results of a test made on representative samples of illuminating kerosine. In this a severe overdose of the antistatic additive was applied, and in addition the influence of various dosages of the Cr–AC part of the additive was studied.

TABLE X

*The Effect of Antistatic Additive on Specification Properties of Motor Gasoline*

| Tests | Motor gasoline | |
|---|---|---|
| | Without additive | With 3 p.p.m. additive |
| Sp. Gr. 60/60° F | 0·740 | 0·742 |
| T.E.L. ml/I.G. | 1·51 | 1·52 |
| IP gum, mg/100 ml | 4 | 3 |
| Total sulphur, % wt | 0·024 | 0·030 |
| Induction period, min: | | |
| IP | 375 | 315 |
| ASTM | 450 | 360 |
| Odour | Marketable | Marketable |
| F-1 octane number | 95·2 | 95·2 |
| Reid vapour pressure, lb/sq. in. | 11·2 | — |
| *ASTM Distillation:* | | |
| I.B.P., °C | 31 | — |
| 2% | 41 | — |
| 5% | 47 | — |
| 10% | 54 | — |
| 20% | 67 | — |
| 30% | 78 | — |
| 40% | 88 | — |
| 50% | 97 | — |
| 60% | 109 | — |
| 70% | 127 | — |
| 80% | 145 | — |
| 90% | 164 | — |
| 95% | 176 | — |
| F.B.P. | 180 | — |
| % Recovered | 96·5 | — |
| % Residue | 1·5 | — |
| % Loss | 2·0 | — |

From this table it is clear that up to 6 parts per million of the additive might be used without any adverse effect, so that the proposed dosage of 2 parts per million should be perfectly satisfactory.

As already indicated, it is also desirable to protect a product such as motor gasoline, which may in certain handling operations give rise to explosive vapour mixtures, even though it is safe under normal conditions. It can be seen from Table X that the specification properties for motor gasoline are not affected by the additive. This is all the more desirable, since it may be required to protect certain components of motor gasoline separately.

TABLE XI

*The Effect of Antistatic Additive on Properties of a Product similar to Tractor Vaporizing Oil*

| Test | Without additive | With 3 p.p.m. additive |
|---|---|---|
| Odour | Marketable | |
| Octane No. (F-2) | 54 | 54 |
| *Distillation:* | | |
| I.B.P., °C | 145 | |
| Recovery at 160° C, % vol | 16 | |
| Recovery at 200° C, % vol | 71·5 | |
| F.B.P., °C | 256 | |
| Flash point, Abel, °F | 84 | 84 |
| Total sulphur, % wt | 0·196 | 0·196 |
| Existent gum, mg/100 ml | 1 | 1 |
| Potential gum, mg/100 ml | 2 | 3 |
| Neutralization value, mg KOH/g | 0·001 | 0·001 |

Table XI shows that the specification properties of tractor vaporizing oil types are not affected either.

## CONCLUSION

It can be said that the incorporation in the products of antistatic additive has been proved to provide a means of alleviating the hazards due to static electricity in handling petroleum products. It has been shown that the proposed additive has no effect on the specification properties of white products. Extensive tests are being carried out to investigate whether there are any harmful effects on product performance. The results so far are encouraging.

The use of an antistatic additive does not do away with the necessity for bonding all equipment. If antistatic additive is applied to oil products and if all equipment is bonded, it may well be that pumping rates can be safely increased, not only in the refinery but also when loading tankers.

## ACKNOWLEDGMENTS

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[5] British Patent No. 749,898, in the name of N.V. De Bataafsche Petroleum Maatschappij. Patents have also been taken out in other countries.

## DISCUSSION

**E. S. Squire:** It must be borne in mind that tanks are filled with petroleum products some hundreds of times a day throughout the industry. The number of cases where explosions occur are relatively rare, and of these some are due to causes other than static. The authors list forty-six explosions which can be attributed to static, and probably about half of these can be considered to have been concerned with normal filling of tanks. It is true that some products, even in the white oil category, are safer than others by virtue of their vapour pressure, but it is also true that a very large number of movements of the more dangerous products take place daily without mishap. It must be assumed, therefore, that when explosions are caused by static some very critical combination of conditions has arisen.

I imagine that the authors must have been very disappointed when they failed to produce explosions in their test tank without the introduction of a spark gap, and I feel that this is still a serious weakness in the work. The results would have been far more convincing if the experimental work had shown that, without the additive, explosions could be produced at will without the introduction of artificial devices, explosions being prevented on addition of the additive.

I take it that the authors would agree that the ideal situation would be that the conductivity of the petroleum product was such that the relaxation time was so low that no accumulation of charge would occur in the pipeline or filter, so that no charge entered the tank. This is perhaps too much to hope for, as it would probably require the addition of quite unacceptable quantities of additive.

One asks oneself the question, why did no explosion occur in the course of these experiments in the absence of spark gaps? The critical conditions necessary could not have been present, and without a detailed knowledge of these, we cannot be certain that the addition of the additive would have prevented an explosion under these critical conditions. This has not been demonstrated.

It would be interesting to know whether the authors have any views as to why no explosions took place in the absence of a spark gap.

In other publications the authors point out the complex nature of the electric fields in a tank being filled with oil containing static charges, but they assume that, whatever the intensity of these fields might be in any part of the tank, they will be proportional to the vertical field measured over the centre of the tank above the oil.

Further, in developing a theory of the fields produced in a tank being filled with petroleum products, the calculations have been directed towards obtaining the strength of this vertical field. It would appear that this may not be the significant field to be considered, and that the field most likely to give rise to discharges in the tank might quite well be the field at right angles to this across the surface of the oil. The authors would doubtless agree that charges accumulate on the surface of the oil, and I suggest that what has to be considered are the conditions arising from these charges on the surface of the oil. Whether one considers that the charges are immobile and produce a field in the plane of the surface, or whether the charges are moving across the surface to the earthed shell of the tank, there is a potential gradient across the surface which I believe will be at a maximum at the shell plate, and I consider this is where the danger spot lies. It seems possible that discharges can take place across the surface of the oil, in addition to discharges from the surface to an earthed conductor.

The nature of the surface through which the charges are moving is a little difficult to visualize. At equilibrium, where the total charge entering the tank is equal to the charge leaving, there are electric forces in the system which have resulted in charges accumulating on the surface. In passing from the surface to the shell of the tank, it is quite unlikely that these charges will move from the surface against these forces, and one has, therefore, to consider the movement of these charges through a thin layer near to the surface. This might have properties quite different from the bulk of the oil.

An increase in the conductivity of the oil, while reducing the relaxation time in the bulk of the oil, could also result in charges arriving at the surface at a higher rate, and having to be dissipated to earth along the surface.

One of the critical conditions necessary to produce an incendiary discharge might well be connected with the relationship between the relaxation time of the bulk of the oil and the relaxation time of the surface. It should be pointed out here that even if the conductivity of the oil in the surface is the same as in the bulk of the oil, the relaxation time of the surface will not be the same, as the dimensions which determine its capacity are different from those which determine its resistance, and therefore these do not disappear from the equation for relaxation time.

If the authors had succeeded in producing explosions in the absence of a spark gap and had shown that the presence of the additives prevented the explosions, the above argument would have no force. The criterion that the authors have used in determining the amount of additive that should be used is that the field strength as measured vertically above the surface of the oil at the centre of the tank should be reduced to a very small fraction of the field strength measured without the addition of the additive. Unfortunately, this has to be decided in an arbitrary way.

In the absence of more knowledge and the relation of this field strength to other field strengths which can be present, especially those across the surface of the oil, it seems to be a little unsafe at this stage to rely on this criterion.

With regard to the specific questions arising from the paper: (1) Am I correct in assuming from Table I that the authors have no knowledge of an explosion caused by static when pumping oil into tankage in the absence of water or air in the oil? (2) In view of the extremely small quantities of materials required to produce static phenomena, is it possible that if a product containing the antistatic additive is pumped through a system which previously handled some other product with one of the numerous additives that are now used for various reasons,

would the presence of such an additive adsorbed on the surface of the line in the initial stages of pumping affect the safety that might be conferred by the use of the antistatic additive? (3) In Fig 6 I think the ordinate marked ambient temperature should really be the temperature of the oil in the tank, as the vapour composition near the surface of the oil would be more nearly related to the temperature of the oil than the ambient temperature.

**Dr A. Klinkenberg:** We were asked if we knew of any accident where the oil contained neither air nor water. Assuming that the question refers to an explosion in a grounded container, *e.g.* a refinery tank, the answer must be that we do not know of such an accident. However, we do know of a case which comes rather near Mr Squire's description and which affected us closely in that it initiated the present research into static electricity. I refer to the two accidents we had at Pernis refinery four years ago. The remarkable feature here was that the same sequence of events caused an explosion on two successive days.

A certain blending procedure was being carried out when the tank exploded. The fire was extinguished and the product salvaged and transferred to another tank of the same size and shape. As the blending was not yet finished, it was continued the following day and there was another explosion. This was considered to be a very strong argument in favour of static electricity as the cause of both these explosions, because other possibilities, such as an open fire, sabotage, and lightning, could be effectively ruled out. The product had been treated and contained a treating haze, but it was free from large quantities of water. However, in all the other cases I know of, there are indications that considerable amounts of water, air, sulphuric acid, caustic soda, and the like were present.

During pumping operations from tanks into tankers, and vice versa, most accidents occur at the beginning of the operation, at precisely the time when the product may be contaminated with water from the line. In several cases—offhand I remember a fire at Shell Haven three years ago and, more recently, an explosion in Australia—it is quite easy to deduce that the explosion must have coincided with the arrival of a slug of water at the receiving tank.

I am not, of course, referring in this case to explosions occurring in non-grounded surroundings. There are cases that may be misleading in this respect. I might mention the case of a sampler taking a sample while standing in rubber boots on the roof of the tank. In this case the sampler, the tape, and the sampling can form an insulated conductor, which could be charged in the same way as the wire coil which we had connected to a spark gap during our experiments in Germany. In fact, there is a case on record of a sampler reporting sparks between his sampling line and the tank hatch. Obviously, this is not a case of completely grounded surroundings.

Then there is Mr Squire's question about pumping a product containing an antistatic additive through a system which previously handled some other product with one or other of the numerous additives now being used. I think that this should only serve to improve the situation. If a batch of undoped product is followed through a very long pipeline by material containing antistatic additive, it will probably be found, although we have not yet tested it, that the first barrels of the doped material to arrive at the other end of the pipeline will show depletion of additive. Therefore it is a wise precaution to pump slowly right at the beginning if one feels that the receiving tank might be in danger. But once the pipe wall is saturated with the additive there should be no further depletion. If the preceding batch contains some other additive the same phenomena will occur, but if the other additive has some antistatic properties, as is the case of some of the anti-corrosion additives, the switch-over will be less abrupt. I do not think that the switch-over could become dangerous through the presence of the other additive in the first product. Similarly, if the product containing antistatic additive is followed by a product free from antistatic additive, desorption of the additive from the pipe walls will occur and the undoped product will be found to contain traces of the antistatic additive for some time.

In regard to ambient temperature, I agree that it is the temperature of the liquid in the tank and not the temperature outside the tank which is the determining factor for the composition of the vapours close to the liquid.

Mr Squire said that we mentioned only forty-six explosions, and that this is a very small number compared with the very large number of movements of the more dangerous products taking place daily without mishap. Of course, these forty-six did not refer to the entire oil industry, nor did they refer to Shell only. We have tried to collect as much data from our group as we could find, but the survey is certainly not representative of the entire industry.

Some of these are indeed due to a combination of circumstances, some abnormal handling operation being done or some valve being opened too fast. For instance, in the Australian explosion the rate of flow was temporarily decreased during the switch-over from gasoline to kerosine. Unfortunately, when the rate of pumping was increased again, the interface between the kerosine and the water separating the gasoline from the kerosine was just arriving at the kerosine tank. Moreover, the kerosine happened to be slightly contaminated with the gasoline, sufficient to create explosive conditions in the kerosine tank. Under these circumstances, increasing the flow caused excessive electric charging, which, in turn, led to an explosion.

The necessity of using a spark gap was very disappointing. We have even doubted whether it is actually possible to draw incendiary sparks (or corona discharges) from the surface of an insulator to a conductor near by. However, this point has been re-confirmed, both by workers at Esso and by Dr Nederbragt at our Amsterdam laboratory. In such experiments, an electrode is set over a liquid surface and a strong potential difference applied between the electrode and the liquid. It was also interesting to note that the surface became strongly disturbed, possibly causing local increases at field strength.

The assumption has been questioned that whatever the intensity of the electric fields in a tank might be, in any part of the tank they will be proportional to the vertical field measured over the centre of the tank above the oil surface. This assumption is, of course, uncertain, but one must have some measure of static hazard. It is impossible to measure field strength at exactly the point where the discharge is going to occur. For one thing, it is impossible to measure local field strengths without disturbing the situation and, again, the local field strength may be totally undefined, *e.g.* when the field strength causes deformation of the liquid surface. We feel that measuring the vertical field strength in the centre of the tank is the best thing one can do to have a yardstick for assessing static hazard.

It may well be that the horizontal field strength is the more significant, and we have therefore been developing a horizontal field meter. This consists of a rod with a cylindrical surface which can be covered by rotating

vanes and thus be alternately exposed to the field. In fact, the instrument is based on the same principle as our vertical field meter. This might, for instance, simulate conditions around a thick wire, a swingpipe cable, and so on. Much higher field strengths were found with this instrument than could be obtained with the vertical field meter. We have been measuring field strengths of 2 million volts per meter with the horizontal field meter, about two-thirds of the normal breakdown tension of air.

On the other hand, this does not invalidate the general principle of using the field strength in the top of the tank as a yardstick. If it is true that the whole distribution of charge is changed proportionally if an additive is used, then the vertical and horizontal components of the field strength remain proportional and one is still entitled to measure the vertical field strength only.

Charge collects at the surface, but we have not considered a lateral slow discharge through the surface. In other words, we have considered the space within the tank as being composite, consisting of air and liquid, and we have considered the surface as being a mathematical surface, capable of carrying a surface charge, but not of conducting a current. I think this is an acceptable mathematical picture of physical reality.

In equilibrium there will be a surface charge and there is no need to bring more charge to the surface or to take it away again. Actually, the vertical component of the field strength should become zero immediately below the surface of the liquid. If, therefore, the charge generation is reduced, the excess surface charge will simply leak away through the bulk of the liquid, but any evidence for a separate contribution to relaxation by conduction through the surface is, of course, very interesting.

An increase in the bulk conductivity of the oil might temporarily give rise to an increase of flow of charge at the surface. However, this will only be the case if the conductivity of the liquid is so low that the condition of maximum electrification is not yet reached. In the range in which the conductivity of a doped product will be, a further increase in conductivity will be beneficial for several reasons. First, the current issuing from the pipeline will become smaller. Secondly, the total amount of charge accumulated in the tank will be reduced because for constant current it would already be inversely proportional to the conductivity. So, in this case, increasing the conductivity will temporarily cause an increase of flow of charge away from the surface.

Moreover, there is another argument which contradicts to some extent something that has been said earlier. I have said that if conductivity is varied the whole distribution of charge changes proportionally. Strictly speaking, however, I should have mentioned that the effect of a considerable increase in conductivity would be that the charges introduced with the incoming liquid remain close to the inlet because they can never get very far into the tank in view of the relaxation. At a conductivity of 1000 units the relaxation time is only of the order of $\frac{1}{100}$ second. If one considers a parcel of liquid having this conductivity issuing from the inlet of a tank, one will see that it must have lost practically all of its charge in a few hundredths of a second, and it cannot have travelled very far into the tank in that time. Therefore, the ultimate effect of the anti-static additive will be to keep the charges very close to the inlet and there will be no problem of excessive charge arriving at the surface.

**Major W. F. Howard-Jones:** In any future limited war we in the Army are expecting to use equipment which will enable us to get petroleum lines and storage down in a hurry. At the present time there is no civilian counterpart to give us any idea of what we are up against in respect of static electricity. The possibility of our problems, if any, being solved by the product itself sounds very attractive.

In view of the need to lay down strategic reserves, there is a military requirement for long-life fuels, possibly up to, say, six years in storage. Is it proposed that your tests will be prolonged so that you could say whether the antistatic additive will be effective over that period?

We are also faced with the use of high lead content fuel. Have either of these additives any interaction?

**Dr A. Klinkenberg:** We started our research only four years ago, so we cannot claim to have experience with six years' storage.

There are some points of consolation. The Army does not subject its fuels to the severe conditions which the Air Force may require and, moreover, does not normally filter its fuel. Therefore, the requirements for the antistatic dope are much lower. You would be content to have 20 to 50 conductivity units and if you receive a product having 1000 conductivity units there is a good chance of the product still making the grade after six years. On the other hand, you might consider keeping undoped fuel in storage and adding the dope when the fuel is required. Again, you might obtain doped fuel and, after six years, dope again if necessary.

We did check that there is no interaction effect between TEL and the antistatic additive.

**M. J. Stradling:** Is there not an alternative approach to the static hazard, *i.e.* to construct tanks to rest on insulated beds? The inlet, outlet, and drain lines would also be insulated and each line fitted with a seal to prevent flashback. With the elimination of the path to earth, no discharge would occur. This is a reversal of normal procedure and, therefore, an alternative protection would have to be provided to deal with electrical disturbances in the atmosphere.

**Dr A. Klinkenberg:** Let us consider a tank which is really well insulated. No electricity can leak away through the supports of the tank and the tank is being filled through a line made of a good insulator. The fuel entering this insulating pipeline will have been charged to some extent in the section of the pipeline preceding the insulated part. However, in the insulated line the charge cannot relax, and therefore all the generated charge eventually arrives on the insulated tank, where it cannot leak away. Even if the tank does not start sparking of its own accord, stepping on it for the purposes of gauging or sampling will be unpleasant.

It is very difficult to maintain good insulation under refinery conditions. If the inlet lines are not perfect insulators, but are made from substances such as rubber or PVC, they themselves will also produce charging. It may well be that the cure is more troublesome than the ailment for which it was devised.

**B. T. Fowler:** Three points have been made which I would like to show are interrelated.

Dr Klinkenberg has indicated the hazardous nature of a variety of distillate fuels, in particular jet fuels. In his introductory remarks he also mentioned the beneficial effect of reducing fuel line velocity by increasing pipe size.

Mr Squire has suggested that all residual charges in the fuel should be removed before the product enters a storage tank.

We with Esso have also appreciated these points, and I would like to illustrate where this particular approach has led us.

Experimental work has confirmed that electrical current generated in pipeline flow is given by the following equation:

$$I = (TKV^{1.75})\,(I - E^{\frac{-L}{TV}})$$

where $I$ = current issuing from line with fuel;
$T$ = fuel time constant;
$K$ = factor determined by pipe diameter and fuel pipe interface;
$V$ = velocity;
$E$ = base of Napierian logarithms;
$L$ = pipe length.

The point I want to bring out is that the exponent of 1·75 on fuel velocity $V$ indicates that low linear velocity will keep the charge generation rate down. The factor within the second bracket shows that any charge entering the tank will relax exponentially. This suggests the idea of a relaxation tank wherein line velocity would be reduced and time allowed for charge relaxation.

Normally the last filter on a jet aircraft loading system is on the servicer of refueller truck located directly under the aircraft wing during loading. Thus the fuel passes from the filter at high velocities directly into the aircraft fuel tank with no opportunity for relaxation, and most of the charge generated in the filter would enter the fuel tank. A relaxation tank downstream of the filter would reduce this hazard.

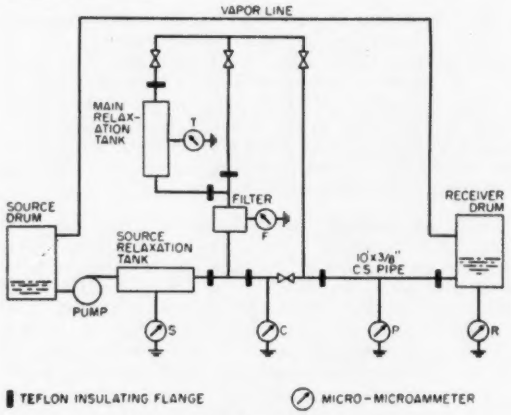


FIG A

CHARGE SEPARATION IN FILTERS

Fig A illustrates our simulated aircraft loading system, where we have three possible paths for the fuel. One is straight along the pipe at the bottom of the figure into the receiver drum. Another goes up through the filter to the receiver, and the remaining route takes in both the filter and relaxation tank.

We have tested several fuels in this rig under a variety of flow rates with three different types of filter elements, and the types of results obtained are illustrated in Fig B.

Graph 1 shows pipeline charge generation alone, and is put in for comparative purposes. Including the filter, as in Graph 2, results in a sharp increase in charge generation which far exceeds the pipeline generation. Although partial relaxation occurs in the pipeline sections, substantial charge still reaches the receiver. When the main relaxation tank is added to the system,

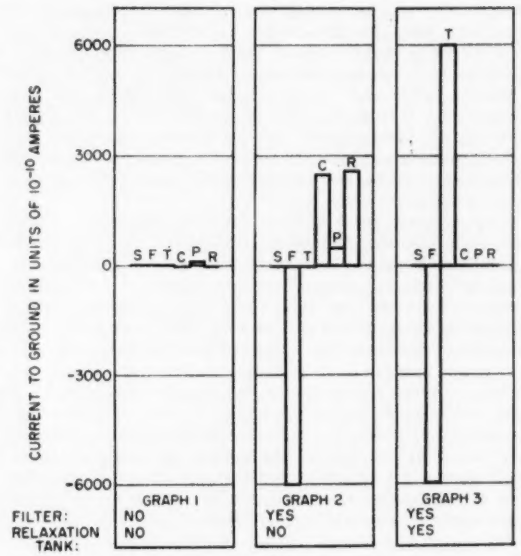


FIG B

CHARGE GENERATION AND RELAXATION IN FILTER TEST

as in Graph 3, all the charge is removed before reaching the receiver.

Calculations based on this type of information indicate that relaxation tanks of a practical size, giving the required fuel residence time, could be installed on a 600 gal/min servicer, and tests are now under way to prove this point. Application of this simple principle should render at least one normal day-to-day operation in the petroleum industry completely free from the hazards of static electricity.

**Dr A. Klinkenberg:** Part of this story I have heard before in Chicago, and some of the drawings are very similar to those in the preprint of a paper by Bustin, Culbertson, and Schleckser, read at the Nov. 1957 meeting of the API. First of all there is the equation describing relaxation, in which the exponential power occurs. I was glad to see that we have all arrived at the same idea of an exponential increase and decrease in the currents. The suggestion was made that the 1·75th power of the velocity has something to do with hydrodynamics. I should, however, like to criticize the equation used by Bustin *et al*, although it is based on their literature reference No. 3, by A. Klinkenberg.

In that literature reference in my paper for the 1955 World Petroleum Congress, I discussed how the ordinary picture of the production of a streaming current in laminar flow can be extended to cover the case where the core of the liquid is turbulent, but where the electric double layer is still entirely within the laminar boundary layer. This is the usual case in colloid chemistry when water or aqueous liquids are used. Combining the electrical behaviour of the laminar sub-layer with the hydraulic behaviour of the turbulent core, one arrives at the relation referred to above, which, by the way, is not my own invention, but has been put forward already by other people, including Mr Fordham Cooper in the U.K. The 0·75 part in the power of velocity is related to the 0·25th power of velocity in the friction factor.

However, we came to realize that in the turbulent flow of hydrocarbon liquids the electric double layer gets so thick that it transcends the laminar sub-layer,

so that actually the electric charges are carried into the turbulent core. In the core the charges are entrained much faster, and thus much higher currents are produced than are even encountered with aqueous solutions at the same velocities.

Consequently, the equation which I gave in the WPC paper is not applicable here. In fact, if one tries to calculate the electrokinetic potential from this equation, one arrives at an impossible result. So it requires a further reasoning that, in the case of turbulent flow, again the streaming current is approximately proportional to the square of the linear velocity of the liquid. We have put forward a suggestion to explain this in our book, when we say that the charging effect in turbulent flow may be expected to be inversely proportional to the thickness of the boundary layer, which, in turn, is inversely proportional to the 7th–8th power of the linear velocity. This, in connexion with the convection effect, which is proportional to the linear velocity, results in the streaming current being proportional to the $1\frac{1}{2}$th power of velocity. Therefore, even though I have been quoted in connexion with this formula, I no longer agree with the way in which it is applied.

The relaxation tank has been mentioned. The relaxation tank could, of course, remove the charge which is produced in the filter, but a new charge will be produced in the pipeline following the tank. So we need only consider the tank for relaxing charges generated in filters.

We have, however, found that such charges can be relaxed quite easily in the lengths of hose which are ordinarily employed between filter and aircraft, provided the conductivity is sufficiently high. Therefore, if all products are being doped, as we believe they should be, there is no field of application left for the relaxation tank.

**Cdr H. D. Nixon:** May I ask the authors whether the additive has any ill effect on the performance of spark ignition engines, after explosion has occurred?

**B. V. Poulston:** It will be realized that it is very difficult to give a straight yes or no to that particular question. One could talk for a long time on the performance of the spark ignition engine itself, and the possible effects of additives on its performance. I can say that we are anxious to know whether an additive of this nature, in the very minute concentrations in which it is proposed to use it, affects the performance of the fuel in the engine. This effect is quite apart from that on the specification tests, which we have covered in the text of the paper and shown to be nil. The collection of this kind of performance information is a very long and intricate process, which is not finished yet. When it is finished, we will be glad to give the answers. I can say, at the moment, that the results are encouraging, but would make it clear that we are going into every aspect of this matter.

**J. H. McGuire:** I would like to preface a technical enquiry with a very sincere expression of welcome at the advent of the Shell antistatic additive. Many workers who are interested in fire and explosion hazards have known for some years that an attempt to increase the conductivity of petroleum and similar fuels is the only completely satisfactory approach to the problem.

My technical enquiry concerns the three categories A, B, and C to which Dr Klinkenberg referred. He said that low conductivity liquids are safe in that little charge is generated. With category B, the intermediate range, there can be a hazard, since the rate of generation of charge is much greater and the conductivity values are still not sufficiently great to dissipate the charges and keep down the potentials. Now, with category C, why is it that the two processes are not stepped up equally and that there is not a greater hazard? The conductivities in the category C range can, we learn, be produced by a concentration of additive as low as two parts per million. Thus, the ions responsible for the level of conductivity are still widely separated in molecular terms, and it cannot be said that conditions are completely different, as would be the case if we considered a metal.

**Dr A. Klinkenberg:** When Mr McGuire says that the conductivities are still so low, I think that we should keep in mind that the amounts of charge we are dealing with are also extremely low. We are talking about charges in hydrocarbon liquids of a few microcoulombs per cubic metre and currents of, at the most, the order of 10 microamperes. An ordinary bulb at 100 volts already carries a current of 1 ampere. We are working in a range quite different from that usually employed in electrical techniques.

The query is: why does one get a maximum in the electrification if the conductivity is increased, and why does the curve go down again?

If a liquid flows in a stationary state in a pipe, there must be a continuous generation of charge at the pipe wall, since there is also continuous relaxation.

Professor Luther, from the Technische Hochschule, Brunswick, Germany, has supplied data to show that when the conductivity is raised, the generation of electricity charge goes on increasing far beyond the figure I have mentioned as a limit of categories B and C. However, what will happen in a pipe? In reply to Mr Fowler, I explained the concept of charges getting in the turbulent core and being entrained there. But if the charges are uniformly distributed by the turbulence over the entire core of the liquid, they will create a very strong electric field. It can be calculated that there must be potential differences of the order of 1000 volts between the axis and the wall of the pipe. Therefore, if the liquid has a high conductivity it is impossible for this charge distribution to the maintained, and there is strong relaxation back to the pipe wall.

Therefore, although the actual generation of electricity at the pipe wall goes on increasing with increasing conductivity, the relaxation within the pipe also becomes even more important. Finally, the rate of increase in relaxation overtakes the rate of increase in generation of electricity, so that the current emerging from the pipe passes through a maximum with increasing conductivity.

However, although the current at 1000 picomho/m may, under certain conditions, still be fairly high, there is yet another effect. In the stationary state the charge collecting in a receiving vessel at the end of a pipe will equal the current in the pipe times the average holding time of electricity in the tank. The latter happens to be the relaxation time. So the product of the current and the relaxation time is the total charge in the tank. But the relaxation time is inversely proportional to the conductivity of the liquid, and therefore the total charge in the tank drops rapidly with increasing conductivity.

Thus the increasing conductivity has a double effect. The charges generated at the wall are for the most part carried rapidly back to the wall and do not even emerge from the pipe. If they do enter the tank, they are so rapidly conducted to the tank wall that there cannot be any considerable accumulation of charge.

A vote of thanks to the authors was accorded with acclamation.

# THE ACCURATE MEASUREMENT OF THE VISCOSITY OF LIQUIDS

A SYMPOSIUM on the Accurate Measurement of the Viscosity of Liquids, arranged jointly by the Institute of Petroleum and the British Society of Rheology, was held on Friday, 6 June 1958, at 61 New Cavendish Street, W.1. The meeting was under the chairmanship of W. Pohl (Chairman IP Sub-Committee 6, lubricants) and Professor E. G. Richardson (President of the British Society of Rheology).

Seven papers were read and discussed and a collection of research instruments exhibited. A visit to the viscometry, chronometry, and thermometry sections of the National Physical Laboratory, Teddington, was made on Saturday morning, 7 June.

The revised Standard Methods (BS 188 : 57 and IP 71/58) of determining the viscosity of liquids in c.g.s. units, which incorporate the experience and the results of co-operative experimental work obtained in the U.K. and other countries during the post-war years describe a "step-up" procedure for the calibration of several glass capillary-type viscometers of approved design and construction, using master viscometers and freshly distilled water at 20° C, with an agreed viscosity of 1·002 cP (1·0038 cS) as sole standard.

At the First World Petroleum Congress held at the Imperial College of Science, London, 1933, the opinion was expressed by Dr Guy Barr of the National Physical Laboratory that the international standardization of viscosities should be made with viscometers of known characteristics rather than by the use of liquid oil standards, as the calibration constant of an instrument is much less likely to change than the standard viscosity oils. This view is maintained in the U.K. at the present time by the viscosity committees of the BSI and of the IP. In the U.S.A. standard viscosity oils are available for the purpose of calibrating instruments, yet it is noted that in the programme of research of the newly-formed rheology section of the National Bureau of Standards efforts are to be directed to the design of a viscometer with which the viscosities of standard oils could be measured routinely without reference to any material standard. The standard methods using glass capillary type instruments are not absolute methods in the sense that the viscosity in c.g.s. units can be calculated from the dimensions of the instrument, and it is necessary to calibrate each viscometer before use in routine measurements.

The instruments described in the standard methods are given a nominal instrument constant in the tables, for convenience in selection, but there is an actual divergence from the nominal with each instrument after manufacture due to the tolerance in dimensions and capillary end effects, etc., and the divergence must be determined experimentally. It is not impossible for the manufacturer to produce a viscometer with the correct nominal constant by adjustment of the fiduciary markings, but the cost would be considerably enhanced.

The problem of designing an absolute viscometer was considered in a paper entitled "The Determination of Viscosity by the Oscillating Vessel Method," by Dr R. Roscoe (King's College, Newcastle upon Tyne). He pointed out that considerable difficulty is encountered in making accurate absolute measurements of viscosity. The only published measurements on a liquid with low viscosity for which a reasonable degree of precision can be claimed appear to be those of J. F. Swindells, J. R. Coe, and T. B. Godfrey (*J. Res. Nat. Bur. Stand.*, 1952, **48**, 1), who determined the viscosity of water at 20° C as 1·0019 $\pm$ 0·0003 cP. The quoted error of 3 parts in 10,000 is the standard error of the mean result, so there is a chance of 1 in 3 that the actual error may exceed this amount, and hence even this very careful determination cannot be regarded as the last word in accurate viscometry. The capillary tube method was used for this measurement, and the error in the result is principally due to the uncertainty of the end-correction. It is well known that the end-correction can always be eliminated by working with two long tubes of different length but of the same radius and using the same rates of flow in each, provided the ends of the tubes are identical. When the results of Swindells, Coe, and Godfrey are treated in this way, however, the results obtained with different pairs of tubes are not quite consistent, and this must be attributed to very small differences in the ends of the paired tubes. There seems to be no way of getting over this difficulty, short of obtaining perfection in the manufacture of the tubes.

It is therefore worthwhile considering an altogether different method for absolute measurements. It was pointed out by Professor E. N. da C. Andrade and Y. S. Chiong (1936) that the oscillating vessel method (originally due to Helmholtz and Piotrowski) could be used for precise determinations, although they claimed an accuracy of only about one part in 500 for their own measurements. In this method the liquid is contained in an axially symmetrical vessel which is held by a bifilar or other torsional suspension and is set in rotation about a vertical axis. The viscosity can be calculated from the logarithmic decrement and time period of the oscillations, the shape and dimensions of the vessel, and its moment of inertia. Andrade and Chiong used a spherical vessel while others, such as M. R. Hopkins and T. C. Toye (*Proc. Phys. Soc.*, 1950, **B63**, 773) have used cylindrical vessels.

This method has several advantages over the capil-

lary tube method: the apparatus is simple to construct, the observations are easy to make, the liquid is contained within a small space (of, say, 5 cm dimensions) so that temperature control is simple and the linear dimensions which have to be measured accurately (*e.g.* the radius of the vessel) are not inconveniently small. Furthermore, no uncertain factor such as the capillary tube end-correction enters into the calculation of the results. On the other hand, the exact mathematical formulæ for the calculation of the viscosity from the observations are too complicated for direct use and have to be simplified by approximations. Andrade and Chiong have given a method of calculation for the spherical vessel in which several small approximations are made at different stages. The method is complicated, however, and it is not easy to see how much these approximations influence the accuracy of the result. In the case of the cylindrical vessel, the method of calculation proposed by Hopkins and Toye is even more complicated, and the effect of the approximations used may be serious.

A new method of calculation has been put forward by R. Roscoe (*Proc. Phys. Soc.*, in course of publication). It may be shown fairly simply that, for any axially symmetrical vessel oscillating with a very short time period ($T$), the logarithmic decrement ($2\pi\Delta$) is given by the relation

$$I\Delta = \frac{1}{4\pi}\int r^2 dS \,.\, (\pi\eta\rho T)^{\frac{1}{2}} \,.\, (1 - \tfrac{3}{2}\Delta - \tfrac{3}{8}\Delta^2 - \tfrac{3}{16}\Delta^3 \ldots)$$

where $I$ is the moment of inertia of the vessel, $\eta$ is the viscosity of the liquid, and $\rho$ is its density. The symbol $r$ is used to denote the distance of an element $dS$ of the inner surface of the vessel from the axis of symmetry, and the integration extends over the whole surface of contact of liquid and vessel. Unfortunately, the accuracy of this formula is only about 10 per cent when a conveniently long time period (say 10 sec) is used with water in a vessel of 5 cm diameter. An accurate treatment has been given, however, for the special cases of spherical and cylindrical vessels. In both of these, the formula given above is found to be modified by the addition of other terms to the series which are dependent upon $\eta$, $\rho$, and $T$, as well as $\Delta$. These terms are given by reasonably simple expressions, and the series converge rapidly under normal conditions.

This and all other theoretical work on the method has been made on the basis of the Navier–Stokes hydrodynamic equations, neglecting the non-linear or "inertia" terms. To take these into account quantitatively would be very difficult, but it can be shown that they must have the effect of increasing the logarithmic decrement at large amplitudes of oscillation. If, however, measurements are made with small amplitudes and it is ascertained that the decrement is constant within the accuracy of observation, it is legitimate to apply the results of this theory.

An experimental investigation of the possibilities of the oscillating vessel method has been made by R. Roscoe and W. Bainbridge (*Proc. Phys. Soc.*, in course of publication), working with water at 20° C. The apparatus was essentially similar to that used by Andrade and Chiong. A major improvement was made by constructing the stem of the spherical vessel out of graduated capillary tubing. The liquid thus acted as its own thermometer, and after calibration the temperature could be read to the nearest hundredth of a degree. The amplitudes of oscillation were measured by eye to the nearest millimetre on a galvanometer scale 300 cm away from the bulb, and a statistical method has been developed for obtaining the best value of the logarithmic decrement from a series of amplitude measurements. The result obtained for the viscosity of water at 20° C was $1{\cdot}0025 \pm 0{\cdot}0005$ cP.

Although the accuracy was not as high as that obtained by Swindells, Coe, and Godfrey, an examination of the sources of error suggests that it could be made appreciably higher by fairly simple modifications. These would include an improved method of measuring the logarithmic decrement, and the use of a cylindrical vessel rather than a spherical one. The inside of a spherical vessel has to be surveyed with extreme accuracy in order to ascertain its departure from exact spherical form and so compute its effective radius, and this is a difficult operation. A similar survey of a cylindrical vessel could be carried out with much greater ease and accuracy.

In the discussion of Dr Roscoe's paper various practical methods of surveying the dimensions of the oscillating vessels and details of the optimum conditions of experiment were described. For example, measurements are made after about 10 minutes oscillation when a steady state had been reached. Using statistical analysis, the precision obtainable could be of the order 1 in 10,000.

M. T. Browne (Imperial College of Science and Queen Elizabeth College) presented a paper entitled "Measurement of Viscosity by an Electronic Counting Technique."

An electronic counting technique suitable for the measurement of the damping of a vibrating body has been described by J. R. Pattison (*Rev. Sci. Instrum.*, 1954, **25**, 490). This apparatus has been modified and applied to the determination of viscosity of fluids. The viscosity is derived from measurements of the damping of a vibrating system immersed in the medium.

A simple measure of damping is the damping capacity $\Delta W/W$ used by O. Föppl (*J. Iron. Steel Inst.*, 1936, **134**, 393; 1937, **135**, 451), where $\Delta W$ is the energy absorbed in each cycle of vibration and $W$ is the total energy of vibration. For small values of logarithmic decrement the following relationship holds

$$\delta \simeq \frac{\Delta W}{2W}.$$

In order to calculate the damping arising from the viscous resistance of the fluid medium it is necessary to evaluate the "surface loading." This is completely specified by the driving point impedance of the medium, $Z_o = \dfrac{\text{amplitude of shear stress}}{\text{particle velocity}}$, which may in general be written $Z_o = R_o + iX_o$. The real component $R_o$ results from a truly resistive force in phase with the particle velocity, while $X_o$ is the out-of-phase component.

Thus, for a rod in torsional free–free vibration, held vertically, and immersed in a fluid medium to a depth $y$, the resultant log dec.

$$\delta_T{}^y = \frac{2\pi R_o}{wl\rho_s}\left[1 + \frac{2}{r}\left(y + \frac{l}{2\pi}\sin\frac{2\pi y}{l}\right)\right] \qquad (1)$$

where $w$ is the angular frequency, $l$ the length, $r$ the radius of the rod, and $\rho_s$ the density of the material.

The relationship between $R_o$ and viscosity has been investigated by Roth and Rich (*J. A. P.*, 1953, **24**, 940). In accordance with their phenomenological point of view all strains in the medium that are in phase with the applied stress result from a single overall rigidity coefficient function $g(w)$, and those $\pi$ out of phase result from a single overall viscosity coefficient function $\eta(w) = \eta$. It is found that for plane shear wave propagation in an infinite viscous medium of density $\rho$, $R_o = \left(\dfrac{w\rho\eta}{2}\right)^{\frac{1}{2}}$. If the liquid is in the form of a thin film some energy may be reflected back from the boundary. If the surface of the film is free,

$$R_o = \left(\frac{w\eta\rho}{2}\right)^{\frac{1}{2}} 1\left[\frac{\sinh 2\theta - \sin 2\theta}{\cos^2\theta + \sinh^2\theta}\right]$$

but if the surface is bounded by a solid material

$$R_o = \left(\frac{w\rho\eta}{2}\right)^{\frac{1}{2}} 2\left[\frac{\cos^2\theta + \sinh^2\theta}{\sinh 2\theta - \sin 2\theta}\right] \qquad (2)$$

$$\text{where } \theta = \left(\frac{w\rho}{2\eta}\right)^{\frac{1}{2}} t$$

and $t$ is the thickness of the film.

A beryllium–copper rod, 12 inches long by $\frac{3}{8}$ inch diameter, held centrally by four screws, is used as the vibrating system and driven in its fundamental torsional mode by the interaction of an alternating current in a coil wound in grooves in the surface of the rod, as indicated in Fig 1, and a transverse magnetic field. A similar coil wound orthogonally to the first acts as a pick-up coil and feeds a decaying voltage to the electronic apparatus when the "drive" is switched off. The electronic apparatus is actuated and counts the number of cycles of vibration ($N$) occurring while the amplitude decreases from one value to half this value. Thus the log dec. $\delta = \dfrac{\log_e 2}{N}$.

The experiments performed with this apparatus have been used to confirm the form of equations (1)

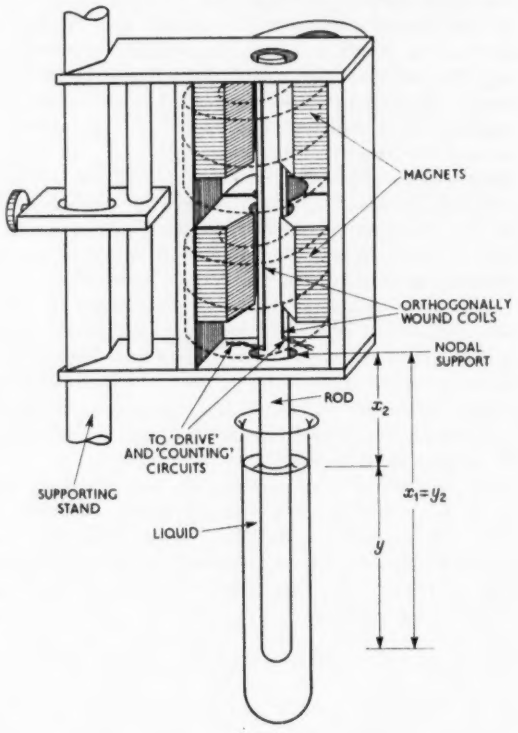


FIG 1

TORSIONAL VIBRATING SYSTEM

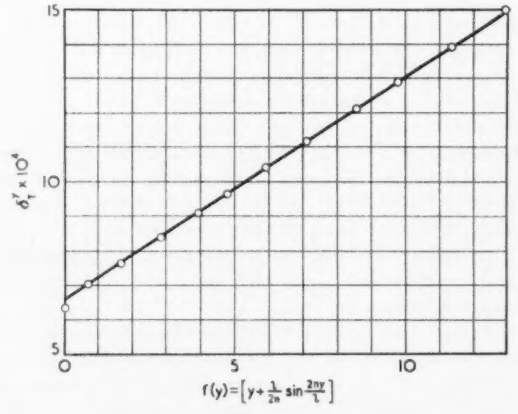


FIG 2

VARIATION OF DAMPING WITH $f(y)$, WHERE $y$ IS THE DEPTH OF IMMERSION

and (2) and to calculate the viscosity function, $\eta$. Fig 2 shows the results obtained by varying the depth of immersion $y$ and plotting $f(y) = \left[y + \dfrac{l}{2\pi}\sin\dfrac{2\pi y}{l}\right]$

against $\delta_T y^2$. The linear graph confirms the functional relationship of equation (1). By imposing a liquid film between the end of the rod and a movable plunger held immediately below this, results have been obtained of damping as a function of film thickness.

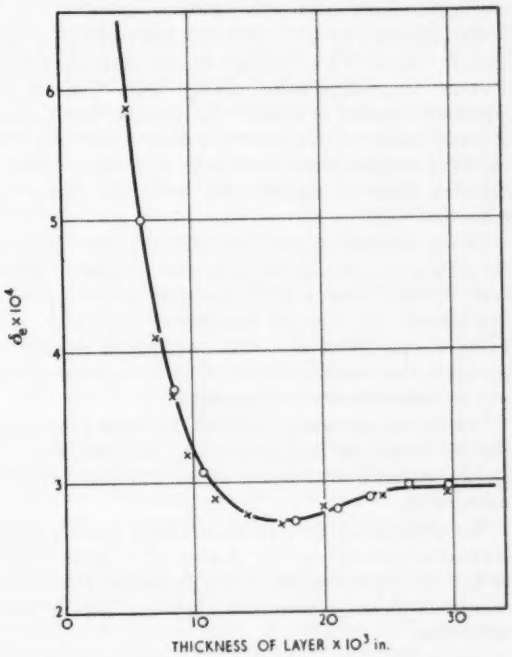


FIG 3

VARIATION OF DAMPING WITH THICKNESS OF "BOUNDED" LIQUID FILM

Plotting the log decrement ($\delta e$) against thickness in Fig 3, these values lie close to the theoretical curve obtained from equation (2) by inserting the accepted value of viscosity. The viscosity of water has been determined by immersing the rod to a depth $y = l/2$, and the results agreed with the accepted static viscosity to within 1 per cent. With a higher viscosity liquid it was only possible to use a small area of liquid. Thus, a drop was located on a plane end of the rod ($y = 0$). This method is rapid and uses only a small quantity of liquid and yet gives results agreeing to within 3 per cent of the standard values. The range of frequency that could be covered by this apparatus, determined principally by the natural frequency of the chosen vibrating system, is of the order 1–100 kc/s.

The apparatus is particularly adapted to measure small changes of viscosity if these can be induced without altering the conditions of the vibrating system. Thus, it is estimated that a 1 per cent change in viscosity could be measured to approximately 5 per cent accuracy.

In the discussion Professor Richardson enquired whether measurements had been made with viscoelastic systems. Mr Browne, in reply, outlined the procedure to ascertain the rigidity component of such systems by using films of varying thickness and noting the variation of damping with film thickness.

It was pointed out that with the more viscous systems results could be obtained using smaller rods and higher frequency.

Industry has become "shear" conscious during the last two decades, mainly in connexion with the requirements of the armed services and the automotive industry. Dr Robert Schnurmann (Esso Research Ltd), in a paper on "Viscosity Measurements at High Rates of Shear," described experiments indicating the effect on the coefficient of viscosity of altering the rate of shear.

At the rates of shear at which viscosities are usually measured the viscosity of liquids does not show variations, but when the rate of shear reaches large values the coefficient of viscosity is no longer a constant; appreciable flow orientation of the molecules takes place with the immediate practical result of a temporary viscosity reduction while the shearing stress persists, accompanied by a decrease of the viscosity–temperature coefficient. If sufficiently large long-chain molecules are in the liquid, high shearing

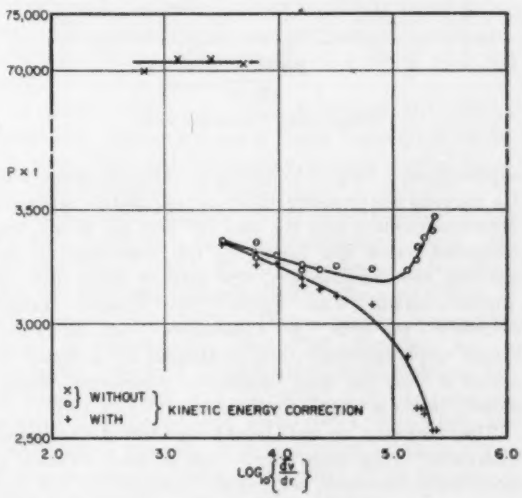


FIG 4

TEMPORARY VISCOSITY REDUCTION OF CASTOR OIL

stresses will bring about a permanent viscosity loss. Under laminar flow conditions it has been necessary to attain rates of shear of more than $1{\cdot}6 \times 10^6$ sec$^{-1}$ to break down molecules of molecular weights of 25,000, whilst larger molecules of molecular weights of 100,000 can already be broken down at mean rates of shear of the order of $10^5$ sec$^{-1}$.

It is important to be able to measure viscosities at these high rates of shear which occur in practice in hydraulic mechanisms and in closely fitting bearings. At these high rates of shear of the order of $10^5$ $sec^{-1}$, experimental conditions must be established so that the sheared liquid suffers no heating, all the mechanical energy being used to shear the liquid. This is an important point because high shearing stresses can be produced by a variety of means, but most of these involve appreciable temperature rise. The complication of heating by friction forces is practically eliminated when a liquid is forced slowly and in individual drops through a narrow streamlined constriction, which behaves effectively like a short

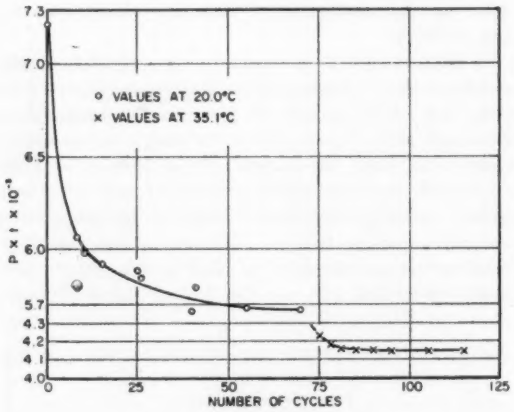


FIG 5

PERMANENT VISCOSITY LOSS

capillary of a length-to-diameter ratio of about 2·5. By varying the pressure difference across this aperture between about 5 mm Hg and 760 mm Hg at a given temperature of the liquid in the reservoir, or by varying the temperature, the rate of shear can be altered within wide limits The kinetic energy correction for this "jet viscometer" can be determined experimentally, and is smaller by a factor of about 2 than for long capillary viscometers, which usually have a length-to-diameter ratio of 100.

The viscosity of any liquid containing elongated molecules—even quite short—can be made to show a temporary viscosity reduction. Castor oil, for example, appears to have a constant viscosity coefficient for rates of shear up to 5000 $sec^{-1}$, yet at a rate of shear of 250,000 $sec^{-1}$ its viscosity is reduced by about 25 per cent.

The apparent viscosity has over a wide range of rates of shear a falling characteristic with a point of inflexion. The curve bends upward when an appreciable proportion of the pressure–volume energy is converted into kinetic energy and when turbulent flow takes place. Thus, to assess quantitatively the temporary viscosity reduction for any particular value of the rate of shear, and to determine the critical Reynolds No., the kinetic energy correction must be applied to the experimental results. It has been shown that the critical Reynolds No. depends upon the length of the largest molecules in the liquid, their concentration, and the rate of shear.

The viscosity of a liquid which has suffered a permanent viscosity loss through severe shearing is more sensitive to temperature change than that of the liquid at low rates of shear. On the other hand, when a liquid suffers a temporary viscosity reduction its viscosity–temperature coefficient is smaller while a shearing stress is applied than when the stress has been removed.

In the discussion that followed, the flow patterns through pipes of liquids, with and without "structure," under various hydrodynamic conditions were considered. In the jet viscometer described, provided the profile of the jet is correct it is possible to calculate the average rate of shear and inertia effects can be determined experimentally.

The frictional heating during the passage through the jet raises the temperature by less than 0·05° C, an advantage not obtained in the rotational type of viscometer.

The instrument is useful in assessing quickly under controlled conditions the degree of "shear breakdown" in a polymer-thickened hydraulic oil: an examination in an experimental test rig usually takes 500 hours.

The subject of the flow behaviour of liquids containing added polymers was continued by Dr P. P. Rutherford (University College of North Staffordshire), who read a paper on "The Measurement of the Viscosity of Polymers at Extremely Low Concentrations."

Viscosity measurements for several polystyrenes in a series of different solvents at 15° and 25° C, using a U-tube capillary viscometer, gave anomalous $\eta sp/c$ and $ln\ \eta r/c$ values at the highest dilutions. For polystyrenes of molecular weight less than 40,000, upswings in the graphs were observed when the above values were plotted against the concentration over the range 0·2 to 0·4 g of polymer per 100 ml of benzene at 25°. The concentration at which these upswings occurred depends on: (*a*) the intrinsic viscosity or molecular weight; (*b*) the temperature; and (*c*) the kind of solvent used.

Control methods and the procedure of precise measurement with results for specially prepared polymers were given; the repeatability was of the order 0·1 per cent.

The flow times for the dilute solutions left in contact with powdered glass for several months were found to be almost unaltered, indicating that adsorption effects are negligible. The anomalous be-

haviour of polymers at low concentration and the dependence of this concentration on the intrinsic viscosity of the polymer are real effects, but before any conclusion can be drawn it is necessary to continue the work, not only by viscosity measurements on a series of fractionated polystyrenes of low molecular weight, but by the measurement of other properties, such as, for example, light scattering and density in the low concentration range.

The paper stimulated an interesting discussion on various aspects of the flow of polymer solutions, and tentative explanations were offered based on observations with several other disperse systems, *e.g.* the orientation of liquid crystals, the restriction of the movement of polymer particles by the walls, electrostatic charge, and adsorption effects. In reply, Dr Rutherford emphasized the need for further systematic work, the peculiar shape of the graphs appearing to negative explanations based on the effect of the walls and of other phenomena mentioned.

After the tea interval a survey of viscometers and equipment used in a modern laboratory was made by K. A. Lammiman and P. R. Morris (Esso Research Ltd) in a paper entitled "The Precise Measurement of Kinematic Viscosity in the Petroleum Industry," which was illustrated with numerous slides and diagrams.

In experimental research work new methods and equipment are constantly being devised to meet the demand of new problems. In routine work, relative rather than absolute viscometry methods are required. The authors first described viscometers for various purposes and the equipment needed in routine analysis, *e.g.* thermostat baths, refrigerating plant, and electronic timing devices, and spoke of the precautions usually taken to ensure the high accuracy specified for viscosity measurements. Pressure jets of various filtered solvents were used for cleaning viscometers between readings. Attention had been given to the precision obtainable with fuel oils by the standard method using the pretreatment prescribed in IP 71/58. Satisfactory agreement had been obtained with the specified precision.

Although no fully automatic measurement in viscometry is yet available, viscometers with built-in platinum probes at the timing marks are now on the market, and the flow times may be recorded automatically.

A description was given of both high and low temperature thermostats and equipment necessary to maintain close temperature control. Where small volumes of oil only are available, miniature capillary-type viscometers are used as well as the plate-cone and other rotary viscometers, and the vibrating reed instrument. It is possible to measure the viscosity of as small a quantity as 0·05 ml by comparing the rate of flow down an inclined capillary with that of a similar quantity of oil of known viscosity.

In the discussion that ensued several recent problems in viscometry were discussed, namely, measurements at very low and high temperatures. A platinum-resistance thermometer was useful for recording temperatures; stirring at high temperatures was effected by a stream of nitrogen.

It was pointed out that the micro method of determining viscosity was beset with surface tension difficulties and was not reliable unless the wetting properties of the oils were similar. In addition, the oil rotates from the walls inwards at the meniscus, so that the oil apparently has a higher viscosity than normal (G. F. N. Calderwood, H. W. Douglas, and E. W. J. Mardles, *Analyt. Chem.*, 1953, **25**, 935). Although it is generally assumed that with the master viscometer the surface tension effects cause an error less than 0·1 per cent, yet it was found that by touching the menisci of water in the viscometer with a surface tension depressant a difference of the order of 0·2 per cent was observed in the flow time in the same way that Dr Guy Barr observed a 1 per cent reduction in a BS routine viscometer (G. F. N. Calderwood and E. W. J. Mardles, *Proc. Phys. Soc.*, 1953, **67**, 395; G. Barr, *Proc. Phys. Soc.*, 1946, **58**, 575). In the standard methods attention is directed to these wetting effects by recommending users to reserve viscometers for the exclusive use of liquids such as silicone fluids, fluorocarbons, etc., which alter the condition of the glass surface.

A short report on "The Standard Methods of Measuring Viscosity in c.g.s. Units" was given by W. Jennings (National Physical Laboratory) and E. W. J. Mardles (Chairman of the Viscosity Panel, IP).

The recommendations of the joint meeting of the IP and the British Society of Rheology, June 1945 (*J. Inst. Petrol.*, 1945, **31**, 26) have been implemented and the practical findings used in the compilation of the revised standards. These specify acceptable types of instruments, course of procedure and a "step-up" method of calibration, rigid cleaning and filtering processes, a high precision in temperature control and timing, and methods of calculating the coefficient of viscosity from flow times, while information is included relating to the effect of air buoyancy, change in gravity, and of other factors.

A reverse flow viscometer for opaque liquids is described, and in BS 188 : 57 a method of procedure for opaque liquids using the ordinary routine viscometers.

The number of routine instruments has been increased; thus, for example, with the BS/U type, eight sizes are given, ranging from A, with a nominal C constant of 0·003 cS/sec, to H, with a C constant of 10, covering a range of viscosity of 1 to 15,000 cS. Five sizes of miniature BS/U viscometers for use

when only limited quantities of liquid are available are also specified.

The instruments are for use over a wide range of temperature; the variation in the constant C due to thermal dimensional changes within the range −80° to 120° C is calculated to be less than 0·1 per cent, and is neglected.

The viscosity committees have endeavoured to avoid, where possible, the difficulty of using the quadratic equation involving $B$, the variable coefficient of the kinetic energy of efflux, for calculating the coefficient of viscosity from flow times. Its use is avoided by choosing longer flow times so that the Second term of the quadratic becomes less than 0·1 per cent. In any case flow times less than 200 sec should be avoided where possible to ensure timing accuracy. The determination of a working value for the coefficient $B$ can be made by the calculation given in the text of the standards, thus avoiding the expense involved in an experimental determination.

A simplified method of determining the coefficient $B$ experimentally is first to evaluate the $C$ constant using an oil giving a flow time greater than 1200 sec, assuming the effect of the coefficient $B$ to be negligible. A short time of flow, as near 200 sec as possible but not less, measured with available oils, is then used to obtain $B$ by substitution of the value $C$ already determined, in the equation,

$$B = ct^2 - \nu t$$

where $t$ is the short time of flow in sec and $\nu$ is the kinematic viscosity of the oil.

An account was given of the results obtained at the National Physical Laboratory when putting into practice the methods of glass capillary viscometer calibration and viscosity measurement given in BS 188 : 57 and IP 71/58. These results are evidence of the satisfactory working of these methods. The accuracy has been assessed by cross-checks with other laboratories. A summary of results obtained during routine calibration of viscometers for industry was included. Observations made, over a period of five years, of the changes with time of the constants of several master viscometers show that the average difference was of the order +0·01 per cent. As an example of the application of the standard procedure to the examination of several oils, the results obtained by several laboratories are summarized in Table I.

TABLE I

*Precision Obtained in Various Laboratories*

| Oil reference | Approx coeff. of viscosity, cS (100° F) | Differences from mean value % | | | | |
|---|---|---|---|---|---|---|
| | | Laboratories | | | | |
| | | A | B | C | D | E |
| Gamma | 3 | −0·10 | +0·06 | −0·01 | +0·06 | — |
| Alpha | 65 | −0·14 | +0·02 | +0·11 | Not tested | — |
| Beta | 390 | +0·05 | −0·11 | +0·06 | Not tested | — |
| Oil A | 8,200 | −0·41 | +0·17 | +0·19 | −0·09 | +0·14 |
| Oil B | 105,000 | −0·47 | +0·32 | Not tested | Not tested | +0·15 |

These results are within the precision specified in the methods.

The meeting concluded with a paper by L. A. Steiner (Viscosity Panel, IP) entitled "Viscometers and Methods of Use," which dealt with the difficulty of using the quadratic equation for calculating the coefficient of viscosity from flow times, the coefficient $B$ varying considerably, and outlined a method for obtaining the true constant of an instrument.

The method involves a set of viscometers of the same design and dimensions with the exception of one variant, the capillary diameter.

The constants of the series are obtained graphically by plotting the inverse of flow times against the ratio of flow times, so obtaining the infinitely large flow time of the family of viscometers. This method is independent of standard liquids.

The author gave graphs showing the regular change of $B$ with flow times and considered that the decrease in the final value was due to the recovery of inertia in the filling bulb during flow. The flow of a liquid in the U-capillary-type viscometer is not in accord with the quadratic equation, and true values for the constant may be obtained only with long flow times.

Mr Steiner then spoke on surface tension and wetting effects and indicated differences in flow times when oils were allowed to stand in the viscometers for different times before testing.

Some oils gave an orange peel effect above the meniscus, and a small but decided change in the flow time occurred. Viscometers designed to neutralize surface tension effects by using the same diameter for the timing and filling bulbs and with long capillaries were exhibited.

The need for using electronic timing devices was discussed.

# PHYSICAL AND CHEMICAL PROPERTIES OF PETROLEUM WAXES *

By W. M. MAZEE †

SUMMARY

Commercial paraffin waxes are mainly composed of *n*-alkanes together with small percentages of *iso*alkanes and/or *cyclo*paraffins and oil.

The straight-chain hydrocarbons show transition points. Above these temperatures the hydrocarbons are plastic; below the transition points they are fairly brittle. The modulus of rigidity is measured to characterize the rheological properties of the wax. The rheological properties are influenced by the presence of the non-straight-chain types of hydrocarbons.

*n*-Alkanes form adducts with urea; this provides the possibility of approximately determining the amount of straight-chain hydrocarbons in commercial paraffin waxes.

Paraffin wax is easily oxidized. This should be avoided in practice because of the bad odour of certain products formed. Addition of small amounts of an inhibitor can successfully retard oxidation.

Microcrystalline waxes are products obtained by crystallization from solvents of certain waxy residues. They are mainly of the *cyclo-* and/or *iso*paraffinic type. Microcrystalline wax is characterized by a high plasticity, which seems to be related not only to the type of hydrocarbon but also to the ratio in which the separate components are present.

THE purpose of the present paper is to discuss a number of physical and chemical aspects of paraffin wax and its components, aspects that are of interest both from the theoretical and practical points of view.

Two quite different types of waxes are available on the market; the usual type of wax, which is predominantly macrocrystalline and is obtained from distillates, and a microcrystalline wax, which is obtained from residues.

## NORMAL COMMERCIAL WAX GRADES

### *Composition and its Influence on Physical and Mechanical Properties*

The usual commercial grades of paraffin wax are mainly composed of *n*-alkanes, which have straight chains, but contain small amounts, between 2 and about 10 per cent, of *iso-* and/or *cyclo*alkanes and some oil.

The physical properties of the separate hydrocarbons in the mixtures are important factors in the behaviour of the wax.

Straight-chain hydrocarbons (21–36 C atoms, the most important range for waxes), all show at least one transition point at not more than about 8° C below their melting points (Table I). The crystal structure changes at this temperature from a more symmetrical form at the temperature just below the melting point into a less symmetrical form at lower temperatures. Sometimes the most symmetrical form is hexagonal, sometimes orthorhombic. Only very few really pure *n*-alkanes have been subjected to X-ray investigations.[1] A complicated behaviour is shown by the *n*-$C_{24}H_{50}$ hydrocarbon. It has a hexagonal form stable between 50·7° and 46·5° C, a monoclinic I structure between 46·5° and 42° C, which may change into a metastable monoclinic II or a stable triclinic form.[2]

The first transition in going down in temperature below the melting point is accompanied by a considerable release of heat; the other transitions usually do not show appreciable heat effects. Some transition temperatures and heats of transition are given in Table I.[3]

TABLE I

| Normal alkane | Melting point, ° C | Transition point, ° C | Total heat of fusion, kcal/mol | Heat of transition, kcal/mol |
|---|---|---|---|---|
| $C_{21}H_{44}$ | 40·2 | 32·5 | 16·8 | 3·7 |
| $C_{22}H_{46}$ | 44·0 | 43·0 | 18·3 | 6·7 |
| $C_{23}H_{48}$ | 47·5 | 40·5 | 19·4 | 5·2 |
| $C_{24}H_{50}$ | 50·6 | 48·1 | 21·0 | 7·5 |
| $C_{25}H_{52}$ | 53·5 | 47·0 | 21·4 | 6·2 |
| $C_{26}H_{54}$ | 56·3 | 53·8 | 23·2 | 8·2 |
| $C_{27}H_{56}$ | 58·8 | 53·0 | 23·1 | 6·9 |
| $C_{28}H_{58}$ | 61·2 | 58·0 | 24·4 | 8·5 |
| $C_{29}H_{60}$ | 63·4 | 58·2 | 24·8 | 7·5 |
| $C_{30}H_{62}$ | 65·4 | 62·0 | 26·0 | 9·0 |
| $C_{35}H_{72}$ | 74·6 | 71·8 | — | — |
| $C_{36}H_{74}$ | 75·9 | 73·8 | — | — |

It is remarkable that the transition temperatures alternate, the even-numbered alkanes having transition temperatures close to their melting points, while in the odd series the temperature differences between melting points and transition points are much larger. The heats of transition also show alternation.

Above the transition temperature the wax crystals are plastic; below this temperature fairly brittle. This is important for the behaviour of the waxes in practice, where some plasticity is very useful.

Mixing various hydrocarbons can lower the transition points, so that the plastic range increases. A striking example of this lowering can be found in the system *n*-$C_{21}H_{44}$–*n*-$C_{23}H_{48}$. Fig 1 shows a heating curve, together with the complete binary system in question. It is seen that the α modifications give a

* MS received 30 December 1957.

† Koninklijke/Shell-Laboratorium, Amsterdam (N.V. De Bataafsche Petroleum Maatschappij).

continuous series of mixed crystals, so that the melting point of $n$-$C_{21}H_{44}$ rises continuously upon addition of $n$-$C_{23}H_{48}$. The transition points show a minimum (at about 23° C) which is far below the

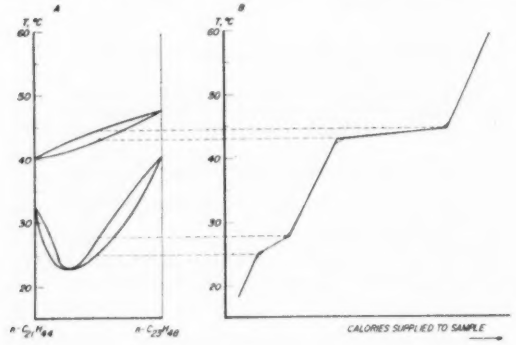


FIG 1

A—$T$–$x$ DIAGRAM OF MIXTURES OF $n$-$C_{21}H_{44}$ AND $n$-$C_{23}H_{48}$
B—HEATING CURVE FOR 50 MOL % $n$-$C_{21}H_{44}$ AND 50 MOL % $n$-$C_{23}H_{48}$

transition points of either of the alkanes. The area in which plastic behaviour of this "wax" is shown is quite considerable, and is contained between the lower part of the melting curve and the lower part of the transition curve.[4]

A similar behaviour is exhibited by mixtures of other $n$-alkanes. Sometimes, however, no lowering of transition points is found, as in the system $n$-$C_{35}H_{72}$–$n$-$C_{36}H_{74}$ (Fig 2).[5]

The mechanical properties of the waxes are important for their behaviour in practice. Unfortunately, the penetration is too often considered a good criterion of the rheological properties of the wax. In the author's opinion, however, the penetration is of little value for this purpose, and the modulus of

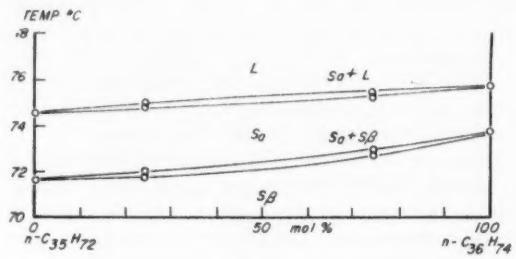


FIG 2

SYSTEM $n$-$C_{35}H_{72}$–$n$-$C_{36}H_{74}$

rigidity is preferred for characterizing its mechanical behaviour.

Consider a bar of wax, of which a cross-section is given in Fig 3. The top part of the bar is subjected to a force at a right angle to its longitudinal axis. After some time the upper part of the wax specimen will have moved over a distance $\Delta l$. If this deformation is propagated uniformly throughout the bar it will be deformed in such a way that its right angles change by an amount $\gamma$. The angle $\gamma$ is called the angle of shear. According to Hooke's law, we may to a first approximation expect proportionality between the shearing stress exerted and the resultant deformation. The angle will then be determined by the shearing force $\tau$ per unit area. Thus

$$G = \frac{\tau}{\gamma}$$

where $G$ is the modulus of rigidity, a shearing stress characteristic of the material. $\gamma$ is easily calculated by dividing $\Delta l$, which is determined in the experiment, by the height $h$ of the sample. A simple

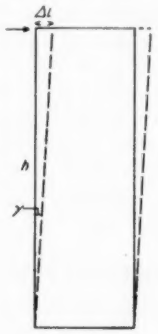


FIG 3

PRINCIPLE OF DETERMINING THE MODULUS OF RIGIDITY

apparatus has been constructed to measure this quantity.[6]

The significance of the modulus of rigidity must now be considered. Table II records some results of the measurement.

TABLE II

| Wax grade | Temp, ° C | Penetration | $G$ in $10^5$ dynes/cm$^2$ |
|---|---|---|---|
| 135/140 wax A | 25 | 15 | — |
| | 35 | 27 | 49 |
| | 40 | 66 | 5·4 |
| 135/140 wax B | 25 | 13 | — |
| | 35 | 30 | 10 |
| | 40 | 54 | 0·68 |
| 140/145 wax H | 25 | 12 | — |
| | 35 | 15 | 110 |
| | 40 | 21 | 55 |

The penetration at 25° C, the temperature at which it is generally determined, shows very little variation. The lowest figure is 12, the highest 15. ASTM method D 1321–54 T mentions a reproducibility of 3 and a repeatability of 2 points at this level. One can hence hardly speak of any difference in penetration

at 25° C. Even the 140/145 wax, which is considered as a hard grade, scarcely shows this hardness in its penetration figure.

At other temperatures also the penetration provides little information. At 35° C waxes A and B have penetration figures of 27 and 30 respectively, which is nearly equal, whilst their moduli of rigidity are quite different; that of wax A is about five times that of wax B. This means that at a given load the deformation of wax B is five times greater than that of wax A; in other words, wax A is deformed to the same extent as wax B under a load that is five times as high. Penetration would not have allowed of any differentiation between waxes A and B, which are of the same grade, but show different rheological properties. The modulus of rigidity is also far more sensitive to temperature, as can be seen from the figures in Table II.

If the 140/145 grade wax H is now compared with the two softer grades A and B, the same lack of information provided by the penetration is found. At 40° C the ratios of the penetration of A and B to H are 3·1 and 2·6 respectively. On the other hand, the corresponding ratios in the moduli of rigidity are 10 and 81, figures which allow of a much clearer differentiation. In other words, at this temperature wax H is 81 times more resistant to deformation than wax B, but only 10 times more than wax A if the same shearing stress is applied.

In accordance with these observations it was, for instance, found that the wilting at certain temperatures of candles made from the various waxes could be predicted from the values of the moduli of rigidity, low values being always paralleled by marked wilting. The penetration did not provide any indication whatsoever in this respect.

Let us now come back once more to the composition of the wax. As stated before, the normal grades of wax consist mainly of *n*-alkanes, a certain percentage of *iso*- and *cyclo*-waxes and a certain amount of oil. The percentage of non-straight-chain hydrocarbons usually varies between about 2 and 10 per cent, the amount of oil between 0·1 and 3 per cent.

What happens when this mixture starts to crystallize? It is clear that the highest-melting alkane present in the mixture will begin to crystallize first. Subsequently, lower-melting components will crystallize around the crystal nuclei already formed. The heterogeneous composition of the crystals is even to be expected in the case of mixed crystal formation. The outside of the crystal will always contain a higher percentage of low-melting components than the nucleus of the crystal. The oil does not participate in the formation of the crystals at all; it is found at the interfaces between the crystals.

A mixture of low-melting straight-chain hydrocarbons can at room temperature be above the transition temperature. It is therefore very plastic, a fact reflected in the value of the modulus of rigidity, which is about 200–500 times as low as that of the higher-melting fraction in the same wax. The *iso*- and/or cyclic waxes show a modulus of rigidity comparable with that of the low-melting *n*-alkanes above their transition points. As the latter low-melting components are found together with the oil on the outside of the harder crystals, they for the greater part determine the behaviour of the total mass. The low-melting waxes and the oil present act more or less as a lubricant. This concept, which could be anticipated from simple considerations on crystallization, was confirmed by torsion experiments on bars of wax and by vibration experiments in which the damping of sinusoidal waves in wax bars was measured.

The fact that the *iso*-waxes have a much lower modulus of rigidity, and can be deformed quite easily, is turned to practical use for making very plastic waxes for certain purposes.

Will it be possible to make a certain wax grade more resistant to deformation or, in other words, can a certain wax be given a higher modulus of rigidity?

A high-molecular-weight microcrystalline wax, which in itself has very small crystals, can decrease the crystal size of a macrocrystalline wax, even when added in a concentration of about 1 or 2 per cent. At a concentration of about 5 per cent, hardly any differences in crystal size can be observed microscopically between a pure microwax and a blend of macro- and microwax.

The modulus of rigidity may be expected to increase on the addition of a small percentage of microwax to the normal waxes. If the crystal size becomes smaller, the total surface area of the crystals will increase and the amount of low-melting waxes will be spread over a larger area, with the result that the thickness of the layer is much smaller. There will be more points of contact between the harder nuclei, and the resistance to deformation will be increased. Table III gives some quantitative data on the effect of adding microwax in a small percentage to a normal grade.

TABLE III

| Wax grade | Temp, °C | Penetration | Modulus of rigidity, $10^8$ dynes/cm$^2$ |
|---|---|---|---|
| 135/140 E | 25 | 12 | — |
| | 35 | 19 | 12 |
| | 40 | 43 | 3·6 |
| 135/140 E + 1% of high-molecular-weight microcrystalline wax (congealing point 82° C) | 25 | 13 | — |
| | 35 | 19 | 46 |
| | 40 | 42 | 11 |

It can be seen that the resistance to deformation at 35° C had become about four times as high when 1 per cent of microwax was added; at 40° C this factor was about three. Again the penetration did not show any improvement as the result of this addition.

It should be noted that certain kinds of high-molecular-weight microwax, when added in larger percentages to normal waxes, may cause a reduction in the modulus of rigidity. If this property is plotted against the percentage of microwax added a maximum is usually found, its position depending on the properties of the two components and their interaction.

*Adduct Formation*

Another subject, and one that has created considerable interest in the past few years, both from a theoretical and practical angle, is the formation of adducts between urea and certain components of wax.

In 1939 Bengen [7] observed that urea could form a kind of compound with certain classes of organic substances, including aliphatic hydrocarbons, alcohols, acids, and ketones. It was observed that a minimum chain length was necessary and that the carbon chain, or a certain part of the chain, had to be straight. Bengen applied for a patent, which he ceded to the IG Farben-Industrie in 1941. When these facts became known after the war, a large number of investigators studied the behaviour of this type of adduct. The adduct between urea and hydrocarbons to which our discussions will be limited can easily be obtained by contacting the hydrocarbon with urea in solution. In the case of the lower hydrocarbons, such as $C_{10}H_{22}$ or $C_{16}H_{34}$, one can simply add the alkane to a solution of urea in methyl alcohol. For members higher in the range the alkane must be dissolved in a solvent, for instance methyl-*iso*butyl ketone, *iso*-octane, or carbon tetrachloride. The adduct precipitates as a crystalline mass.

Analyses of various adducts showed that the ratio between the number of urea molecules and the hydrocarbon is not a whole number. In the case of decane, for instance, this ratio was 8·3 : 1. The normal crystal of urea is tetragonal, but under the influence of a straight-chain hydrocarbon (or alcohol, acetone, or acid) urea crystallizes in a different manner. Careful X-ray examination by various investigators proved that the urea molecule then forms a kind of hexagonal prism enclosing an internal channel.[7, 8] From the inner dimension of the prism it is evident that branched chains do not fit into the channel.[8, 9]

The oxygen atoms lie in the side of the prism. The urea molecules lie on top of each other with 120° clockwise rotation. The elementary cell is composed of six urea molecules and has a length of 11·1 Å. One urea molecule could be said to occupy a space of 1·85 Å.

It was found that one molecule of nonane binds 7·6 molecules of urea; the length of the channel will then be 14·1 Å. The nonane molecule has a length, if stretched, of 11·7 Å. An empty space of 2·4 Å hence remains in the channel.

In the case of tetracosane it was found that one molecule binds 17·8 molecules of urea, the channel being 33 Å long. The $C_{24}H_{50}$ molecule is 30·6 Å in length. Again 2·4 Å of the channel remains empty per molecule. Calculations on the other hydrocarbons show the same free space in the hexagonal channels. The composition of the complexes as a function of chain length can be readily calculated. Taking the alternate carbon–carbon distance as 2·54 Å and the van der Waals radius of the $CH_3$ group as 2·0 Å, the urea–carbon atom ratio is approximately $[0{\cdot}6925(n-1)+2{\cdot}18] : n$, where $n$ is the number of carbon atoms in the straight chain.

A methyl side group (2·31 Å) on an alkane requires a minimum of 10–13 straight-chain C atoms before complexing will occur, whereas an ethyl branching (3·19 Å) requires over 24 C atoms.[10]

The complexes or adducts formed easily decompose with hot water, and the adducts also decompose before melting. Thus a true melting point cannot be found.

The formation of adducts between urea and the straight-chain hydrocarbons (or those with but small branchings) provides us with the possibility of determining these components approximately in commercial paraffin waxes. Such analyses, for example, reveal differences between comparable commercial wax of different origins. On comparing waxes with the same melting points from North American and Far Eastern base materials, for instance, figures for the adduct-forming components of about 80–90 per cent and 95 per cent (or higher) respectively are found; these figures confirm the view that the Far Eastern waxes at the same melting point contain more normal paraffins than the North American.

*Chemical Properties*

The most important chemical property of wax is its reactivity towards oxygen. There is at present little doubt that the oxidation is a chain reaction. The main chain is formed by the following reaction:

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \text{ (peroxy radical)} \quad . \quad . \quad (1)$$
$$ROO^{\bullet} + RH \longrightarrow ROOH \text{ (hydroperoxide)} + R^{\bullet} \quad (2), \text{ etc.}$$

R is the alkyl group. The former reaction proceeds rapidly, the latter much more slowly.

The alkyl radical ($R^{\bullet}$) required for this reaction can be formed in various ways. For instance, on the decomposition of the alkyl hydroperoxide—the first molecular reaction product, which is often present in

very low concentrations—an alkoxy radical and an OH radical may be found.

$$ROOH \longrightarrow RO^{\bullet} + OH^{\bullet} \quad . \quad . \quad . \quad . \quad (3)$$

The $RO^{\bullet}$ or $OH^{\bullet}$ radical may react with an alkane molecule to form an alkyl radical.

$$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet} \quad . \quad . \quad . \quad (4), \text{ or:}$$
$$OH^{\bullet} + RH \longrightarrow H_2O + R^{\bullet}$$

When no hydroperoxide is present the $R^{\bullet}$ radical can probably be formed because a CH linkage is activated by radiation.

$$RH + h\nu \longrightarrow RH^{*}$$
$$RH^{*} + O_2 \longrightarrow R^{\bullet} + OOH^{\bullet}$$

During oxidation, acids having a bad odour are formed. Any oxidation should in practice therefore be avoided.

The following examples can be given to illustrate the importance of the peroxide which may be present in wax.

A commercial wax contained 0·002 per cent of peroxide (determined as per cent by weight of oxygen reacting with HI) absorbed 1 ml of oxygen per g of wax in 130 hours; in the case where the initial concentration was 0·009 per cent the same amount of oxygen was absorbed in 16 hours. The tests were carried out at 100° C.

Traces of aromatic compounds (as demonstrated by u.v. absorption) inhibited the oxidation of an *iso*-wax fraction very actively. The induction period increased from 30 hours to about 250 hours.

A sulphuric acid treatment of wax, followed by an active earth treatment, removes peroxides completely.

Addition of synthetic inhibitors, *e.g.* of the phenolic type, rapidly removes the radicals formed, so that propagation of the reaction is stopped. The inhibitor must be added before oxidation starts, otherwise it is not sufficiently active. The induction period of a good refined wax can easily be increased fourfold by the addition of about 10 p.p.m. of an inhibitor.

## MICROCRYSTALLINE WAXES

Microcrystalline waxes have a very fine crystalline structure and are manufactured from residual slack waxes. The slack wax has to be deoiled by solvent deoiling; sweating is completely impossible for this type of wax. These waxes consist mainly of high-molecular-weight *iso*- and/or *cyclo*-paraffins. The average molecular weight is about 600–700.

They are characterized by a high plasticity, which seems to be related not only to the type of hydrocarbon present but also to the extremely wide range of melting points of these hydrocarbons.

Microwaxes are usually used in the waxed paper industry for laminating two pieces of paper or a piece of paper and a metal foil. It is important for this type of wax to have a good sealing strength; in other words, the force required to pull the two pieces of paper apart should be as high as possible. An example of the sealing strength of a microwax and its fractions, from a crystallized fractionation, measured under certain standardized conditions, is given in the following example:

Sealing strength of microwax, 24 g/cm:

| Fraction No. | M.p., ° C | Sealing strength, g/cm |
|---|---|---|
| 1 | 86·5 | 5 |
| 2 | 76 | 8 |
| 3 | 70·5 | 60 |
| 4 | 64 | 92 |
| 5 | 58 | 92 |
| 6 | 53·5 | 68 |
| 7 | 47·5 | 56 |
| 8 | 41 | 25 |
| 9 | 34 | 4 |
| 10 | oil | — |

Combining fractions 3 and 7 gave a product with a sealing strength of 83 g/cm; fractions 2 and 8, after mixing, gave a sealing strength of 46 g/cm. There is a pronounced maximum in the blends of the fractions mentioned above.

The above results clearly show that there is a close relationship between the composition of a wax and its sealing strength. Our knowledge is at present, however, insufficient to give an explanation for this phenomenon.

Commercial microcrystalline waxes sometimes have a fairly high percentage of straight-chain hydrocarbons. Too high a percentage has an unfavourable effect upon the quality of the wax.

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# THE ACCELERATION OF PITTING FAILURE BY WATER IN THE LUBRICANT *

By L. GRUNBERG † (Fellow) and D. SCOTT †

SUMMARY

The effect of water content of the lubricant on the incidence of pitting type failure of ball bearings was studied using the four ball rolling test. Several oils of different characteristics which are being used for the lubrication of ball bearings in practice were tested under four conditions of water content. The presence of water in the lubricant accelerated the pitting failure of balls made of conventional EN.31 steel, but had no effect on the pitting failure of stainless steel balls. Microscopic investigations of the initiation of damage to balls under different lubricant conditions are described. The results are discussed, and it is suggested that strict precautions should be taken to prevent the contamination of lubricants with water.

## INTRODUCTION

THE attention of this laboratory was drawn to the premature failure due to pitting of some large ball races which had been fitted to appliances operating in the open with very little shelter. Penetration of water into the lubricant was suspected, but it was yet unknown whether or not this could accelerate pitting failure. It is known already that the nature of the lubricant had some influence on this type of failure (Barwell and Scott,[1] Cordiano, Cochran, and Wolfe [2]). No definite information is at present available on all the physical and chemical properties of the lubricant which are involved. The viscosity of the lubricant was found to affect pitting to some extent, but other factors appeared to have a predominant effect. In view of the environmental conditions surrounding the application, it seemed useful to ascertain what effect the presence or absence of water in a lubricant had on the occurrence of pitting in ball bearings. The four ball rolling test, which had been developed in the Mechanical Engineering Research Laboratory and which in many experiments had proved a useful means of discriminating between lubricants, was employed for this purpose.

## APPARATUS

The four ball rolling test has been described by Barwell and Scott [1] and Scott [3] and uses essentially a four ball lubricant testing machine modified so that the three lower balls are allowed to rotate in a specially designed lower race to simulate the combination of rolling and sliding experienced in angular contact ball bearings (Fig 1). The criterion used is the time which elapses between the start of the test and the first appearance of a pit in the running track of the top driving ball. This test method shares with the normal four ball test the advantage of reproducible and cheap specimens in the form of commercial $\frac{1}{2}$-inch diameter steel balls (EN.31 1·0 per cent carbon, 1·5 per cent chromium, approx 900 V.P.N.). In order to investigate whether or not the presence of water in the lubricant could be associated with corrosive action, stainless steel balls (12 per cent Cr type, hardened, approx 750 V.P.N.) were used in a number of tests.

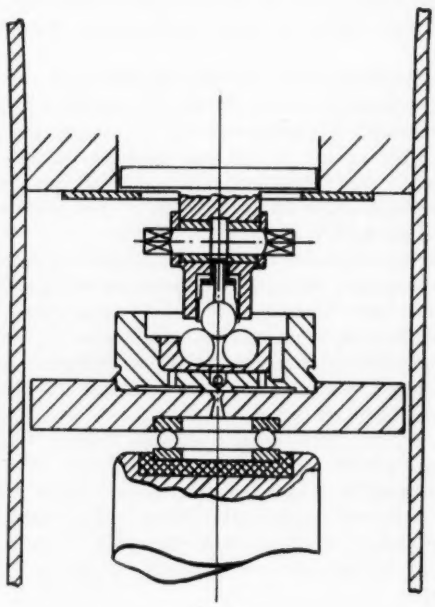

FIG 1

ARRANGEMENT OF THE FOUR BALL ROLLING TEST RIG

## METHOD OF TEST

Four new balls were normally used in each test with bath lubrication, the lower race and holder forming the lubricant bath, which contained 16 ml of the lubricant to be tested. All tests were carried out under axial load of 600 kg (nominal maximum Hertz-

* MS received 22 May 1958.

† Lubrication and Wear Division, Mechanical Engineering Research Laboratory, D.S.I.R., Thorntonhall, Glasgow.

ian stress about 500 tons/sq. inch) at 1500 rev/min. Provision of automatic stopping of the test at the onset of pitting was found to be sufficiently effective to permit immediate detection of the presence of even a very fine surface pit. The appearance of the latter causes slight vibration, sufficient to operate a micro-limit switch.

*Materials Tested*

Several service oils of different characteristics which are being used for the lubrication of ball bearings in practice were examined. Details of the oils investigated are given in Table I.

TABLE I

| Code letter | Spec. | Type, composition, and description of lubricant | Viscosity at 20° C, cS |
|---|---|---|---|
| A | OC. 600 | Compounded oil containing 94% mineral oil and 6% refined rape-seed oil. | 2200 |
| B | OC. 160 | Compounded oil containing 90% mineral oil and 10% blown rape-seed oil. | 600 |
| C | OM. 33 | A refined mineral oil containing 0·5% tricresyl phosphate as an anti-wear additive. Anti-oxidant, anti-corrosive, and anti-foam additives may be present. | 75 |
| D | OEP. 38 | An E.P. oil to specification C.S. 2901F containing extreme-pressure additives. | 90 |
| E | D. Eng. R.D. 2472 | A mineral oil formulated for use in aircraft engines. | 200 |

*Change of Water Content of Lubricant*

It seemed important to vary the water content of the oils between wide limits, so as to include both the condition of extreme dryness and that of supersaturation which might be encountered through gross contamination of the lubricant during running. The lubricants were therefore tested under four conditions of water content:

*I. Dry.*—The oil was dried over metallic sodium for 24 hours before test.

*II. As Received.*

*III. Saturated with Water before Test.*—A sample of the oil was thoroughly shaken with an equal volume of water then allowed to settle 24 hours. The oil was carefully decanted for the test.

*IV. Supersaturated with Water during Test.*—To ensure excess water during test a small quantity (1 ml) was added to the lubricant bath immediately after the start of each test.

The moisture content was determined by the Karl Fischer method [6] on average samples of the oils in conditions I, II, and III before the test, and in condition IV after the test. Table II gives the data obtained.

TABLE II

*Water Content of Oils (% W/W) after Various Treatments*

| Oil | Condition | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| A | 0·01 | 0·027 | 0·15 | 6·86 |
| B | Nil | 0·022 | 0·034 | 3·83 |
| C | Nil | 0·052 | 0·060 | 6·80 |
| D | — | Nil | Nil | 5·63 |
| E | Nil | 0·033 | — | 5·11 |

The E.P. oil D behaved in a rather unusual manner in that no water content could be determined except after supersaturation during the test. It appears possible that the additive present either interfered with the chemical estimation or suffered hydrolysis, which process removed the water. In view of this rather unusual behaviour this oil was not subjected to the sodium treatment.

## RESULTS

The results obtained with commercial EN.31 steel balls as test specimens are summarized in Table III. Those obtained with stainless steel balls are summarized in Table IV.

TABLE III

*Tests with EN. 31 Steel Balls as Test Specimens*

| | | | | | |
|---|---|---|---|---|---|
| Lubricant A | Conditions | I | II | III | IV |
| | Mean life (minutes) | 157 | 124 | 123 | 61 |
| | Standard deviation | 33 | 29 | 33 | 24 |
| | Coefficient of variation, % | 21 | 23 | 27 | 39 |
| | No. of tests | 6 | 9 | 7 | 8 |
| Lubricant B | Conditions | I | II | III | IV |
| | Mean life (minutes) | 123 | 110 | 102 | 54 |
| | Standard deviation | 27 | 27 | 30 | 18 |
| | Coefficient of variation, % | 22 | 25 | 29 | 33 |
| | No. of tests | 7 | 9 | 7 | 5 |
| Lubricant C | Conditions | I | II | III | IV |
| | Mean life (minutes) | 82 | 62 | 54 | 36 |
| | Standard deviation | 27 | 16 | 13 | 5 |
| | Coefficient of variation, % | 33 | 26 | 24 | 17 |
| | No. of tests | 6 | 8 | 6 | 4 |
| Lubricant D | Conditions | I | II | III | IV |
| | Mean life (minutes) | — | 53 | 47 | 16 |
| | Standard deviation | — | 10·5 | 12 | 3 |
| | Coefficient of variation, % | — | 20 | 26 | 19 |
| | No. of tests | — | 6 | 5 | 7 |
| Lubricant E | Conditions | I | II | III | IV |
| | Mean life (minutes) | 107 | 60 | — | 34 |
| | Standard deviation | 36 | 11 | — | 8 |
| | Coefficient of variation, % | 34 | 18 | — | 24 |
| | No. of tests | 12 | 35 | — | 6 |

*Examination of Failed Test Balls*

After the completion of tests the upper (driving) balls were microscopically examined in order to establish whether or not differences in water content had affected the appearance of the running tracks and failure pits. With the oils A, B, and E the surface of the tracks on EN.31 steel balls was bright and contained a single small failure pit, quite independently

TABLE IV

*Tests with Stainless Steel Balls*

| | | | | | |
|---|---|---|---|---|---|
| Lubricant A | Condition | I | II | III | IV |
| | Mean life (minutes) | 34 | 35 | — | 31 |
| | Standard deviation | 8 | 10 | — | 7·5 |
| | Coefficient of variation, % | 24 | 29 | — | 24 |
| | No. of tests | 5 | 10 | — | 14 |
| Lubricant D | Condition | I | II | III | IV |
| | Mean life (minutes) | — | 16 | — | 16 |
| | Standard deviation | — | 4 | — | 5 |
| | Coefficient of variation, % | — | 25 | — | 31 |
| | No. of tests | — | 8 | — | 5 |
| Lubricant E | Condition | I | II | III | IV |
| | Mean life (minutes) | 33 | 32 | — | 33 |
| | Standard deviation | 14 | 5·5 | — | 1·5 |
| | Coefficient of variation, % | 42 | 17 | — | 5 |
| | No. of tests | 7 | 12 | — | 6 |

FIG 2

TYPICAL FAILURE PIT IN THE BEARING SURFACE OF AN UPPER EN.31 STEEL BALL (× 100)

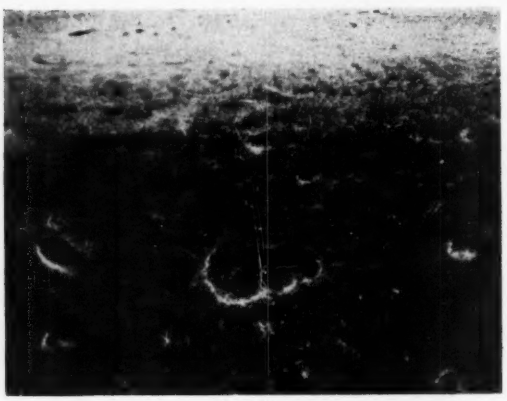

FIG 3

ROUGHENED, STAINED TRACK OF AN UPPER BALL AFTER TEST WITH LUBRICANT C, SUPERSATURATED WITH WATER (× 100)

of the water content of the lubricant (Fig 2 (×100)). Oils C and D, which contained additives likely to attack the surface, gave stained or dull tracks, and in

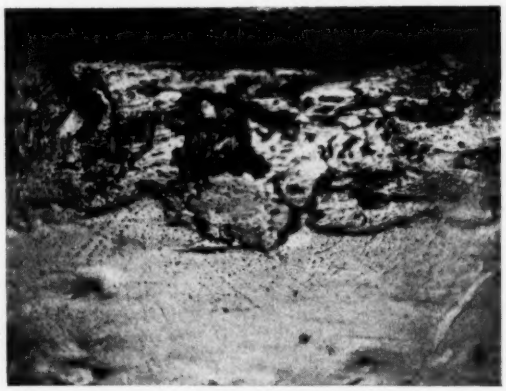

FIG 4

CONTINUOUS TYPE PITTING FAILURE PRODUCED BY LUBRICANT D, SUPERSATURATED WITH WATER (× 100)

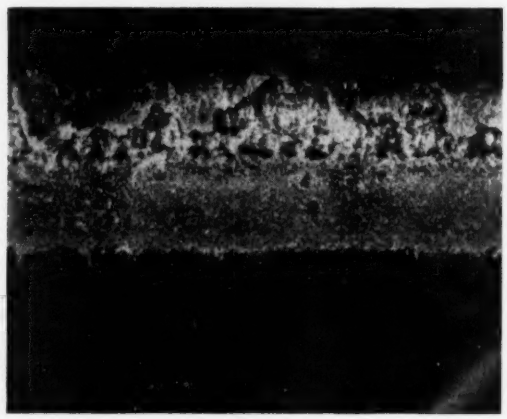

FIG 5

CONTINUOUS TYPE PITTING OF A RACE EXPERIENCED IN PRACTICE WHEN USING LUBRICANT D CONTAMINATED WITH WATER

these instances supersaturation with water produced roughening of the surface (Fig 3, ×100, Oil C, condition IV; Fig 4, ×100, Oil D, condition IV). The roughening or continuous type pitting suggestive of corrosion fatigue may be likened to the damage experienced in practice when using the same lubricant contaminated with water (Fig 5).

The non-corrodible steel balls, except with Oil D in condition IV, had generally bright bearing surfaces containing fine transverse cracks (Fig 6, ×100), which can be regarded as preliminary to the establishment of a pit (Fig 7, ×100). Again no essential differences were observed in tests with stainless steel balls when mineral oils of different water content were used.

FIG 6

TRANSVERSE CRACKS IN THE BEARING SURFACE OF AN UPPER BALL (× 100)

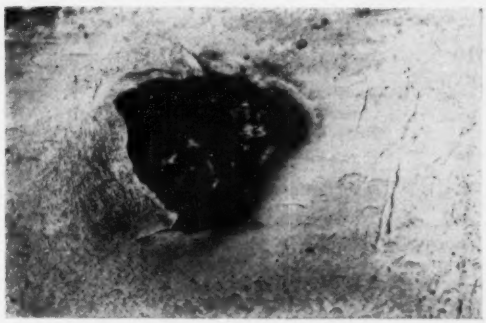

FIG 7

FINE FAILURE IN THE SURFACE OF A STAINLESS STEEL UPPER BALL (× 100)

## DISCUSSION

The experimental results demonstrate that the presence of water in lubricants accelerates pitting failure of ball bearings made of conventional EN.31 steel. Fig 8 shows the effect of water on the mean life of such balls as a percentage of the mean life experienced with the lubricants in the driest possible condition. Whilst removing the small quantities of water normally contained in oils may produce an increase in mean life of the order of about 10 per cent, gross contamination with water, particularly during running, can easily halve the mean life. With non-corrodible steel balls the effect practically disappears. Such balls, however, have inherently such a short life that no advantage can be gained by their use under conditions in which gross contamination of oils may occur.

The statistical fluctuations of the test results may have several causes, one of which appeared to be the variability of the test balls. Owing to the limited supply of stainless steel balls, repeat tests were sometimes made with the same four balls, the upper ball being inverted in the chuck so as to present a fresh surface to the rotating lower balls. Times to failure obtained with the same upper ball and the same lubricant were invariably identical, although there was considerable scatter between different balls, thus suggesting that the variability of the test specimens was an important cause of the fluctuations. Again, if the same upper ball was used to test different lubricants or lubricants of different water content, times to failure were usually in the same ratio as the average results for all tests.

Whilst the effect of water content of the lubricant on the time to pitting is clearly demonstrated by the present experiments, the cause of this phenomenon is not clear. The first manifestation of damage to the materials is the appearance of fine cracks (see Fig 6). These cracks propagate, appear to join up, and cause the local formation of a pit. Whilst nothing definite is known about its effect on these processes, the important effect of environment on fatigue of metals has been studied for many years. Gilbert [4] lists

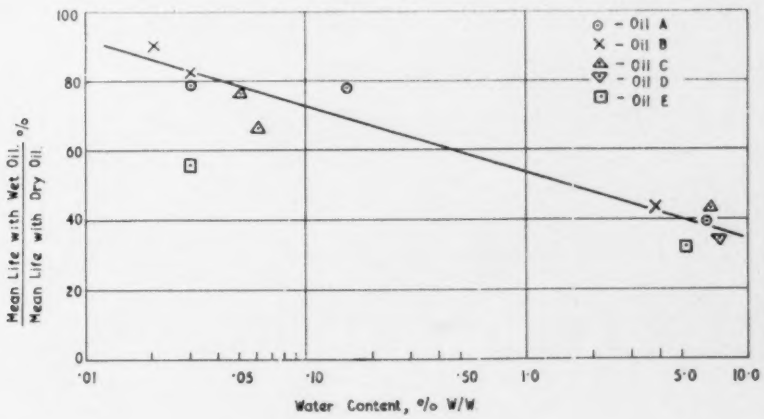


FIG 8

EFFECT OF WATER CONTENT OF THE LUBRICANT ON THE MEAN LIFE OF BALLS

references dating from 1917. Rebinder,[5] in his fatigue studies, suggests that adsorption plays an all-important part. He envisaged that a decrease in surface energy of the metal in the presence of adsorbable substances facilitates the increase in surface area which crack formation and propagation entail. This hypothesis, however, does not explain why water should have a very much greater effect than other adsorbates. Neither does it explain the superior resistance of stainless steel to the presence of water.

As an alternative to the adsorption hypothesis one can consider that electrochemical effects akin to corrosion play a part, owing to potential differences arising between areas strained to different degrees. The present tests were, however, of such short duration that no microscopical evidence could be determined for this mechanism. As corrosive environment created by water content affects the results with conventional EN.31 steel balls, but not with non-corrodible steel balls, it suggests, as have several investigators,[3, 7, 8] that corrosion fatigue is an important factor in pitting.

Whatever the mechanism by means of which the presence of water accelerates pitting, the present work suggests that the failure under investigation was attributable to this cause and that strict precautions should be taken to prevent the contamination of lubricants with water.

## ACKNOWLEDGMENTS

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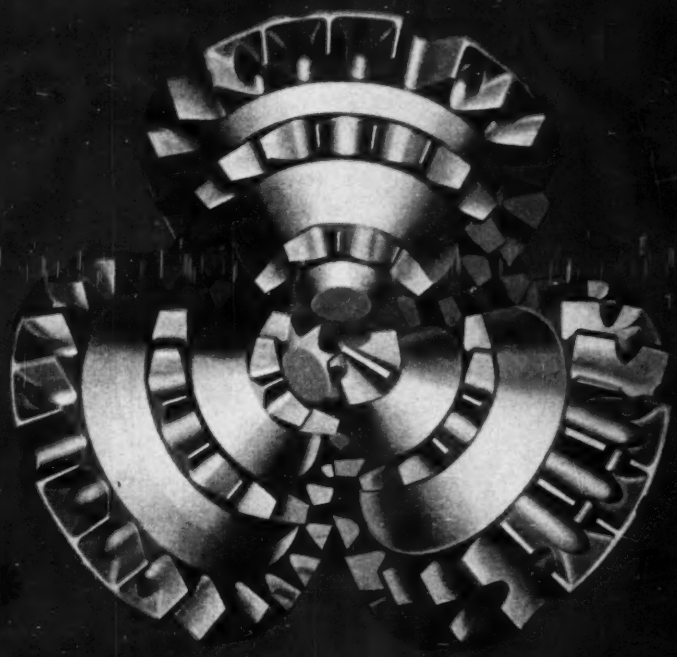

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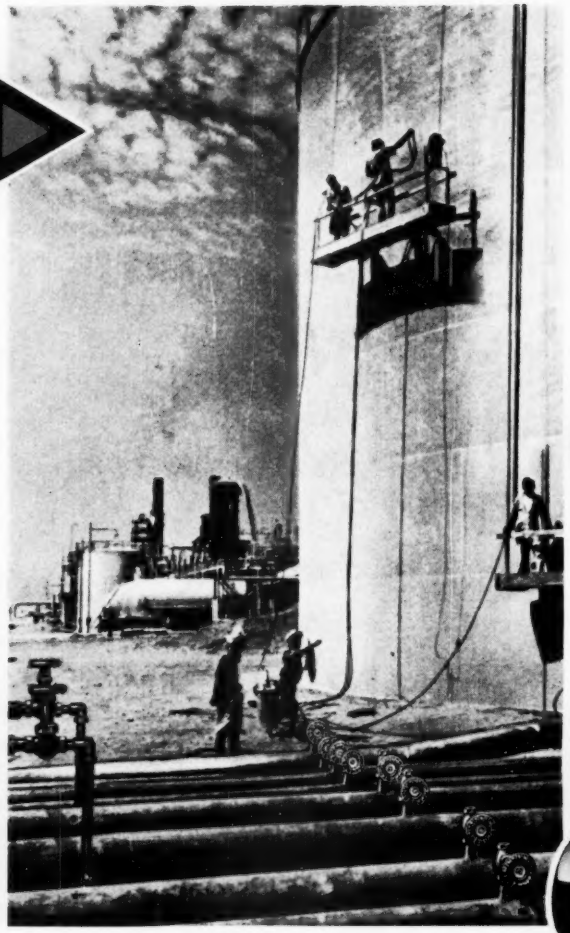

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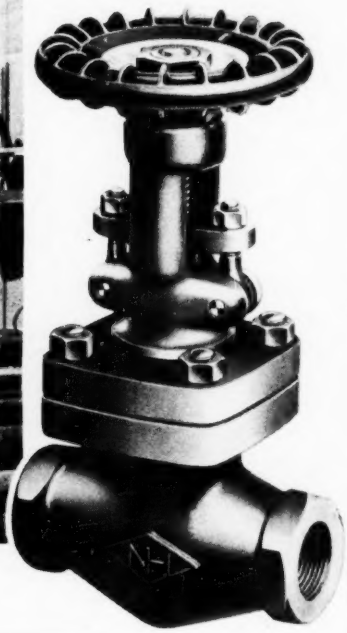

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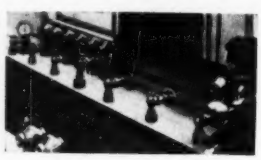

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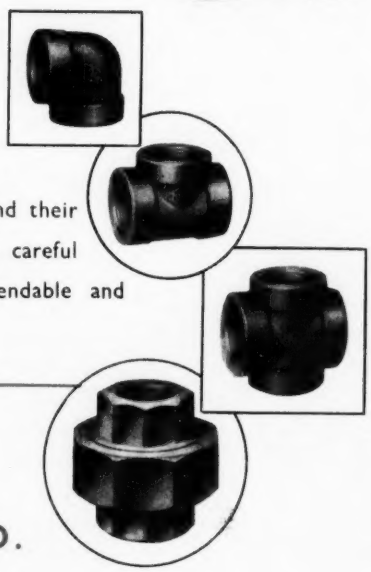

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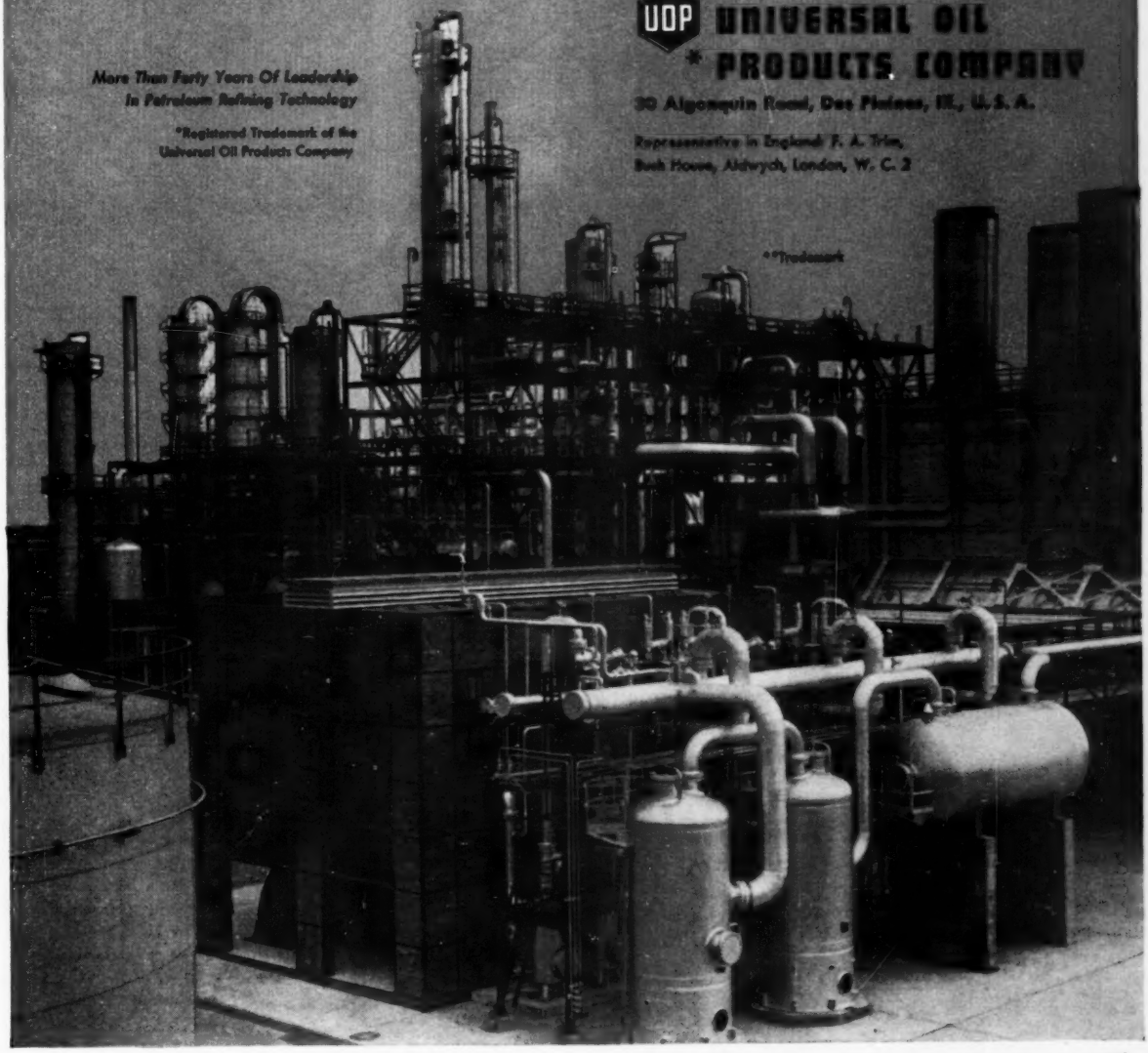

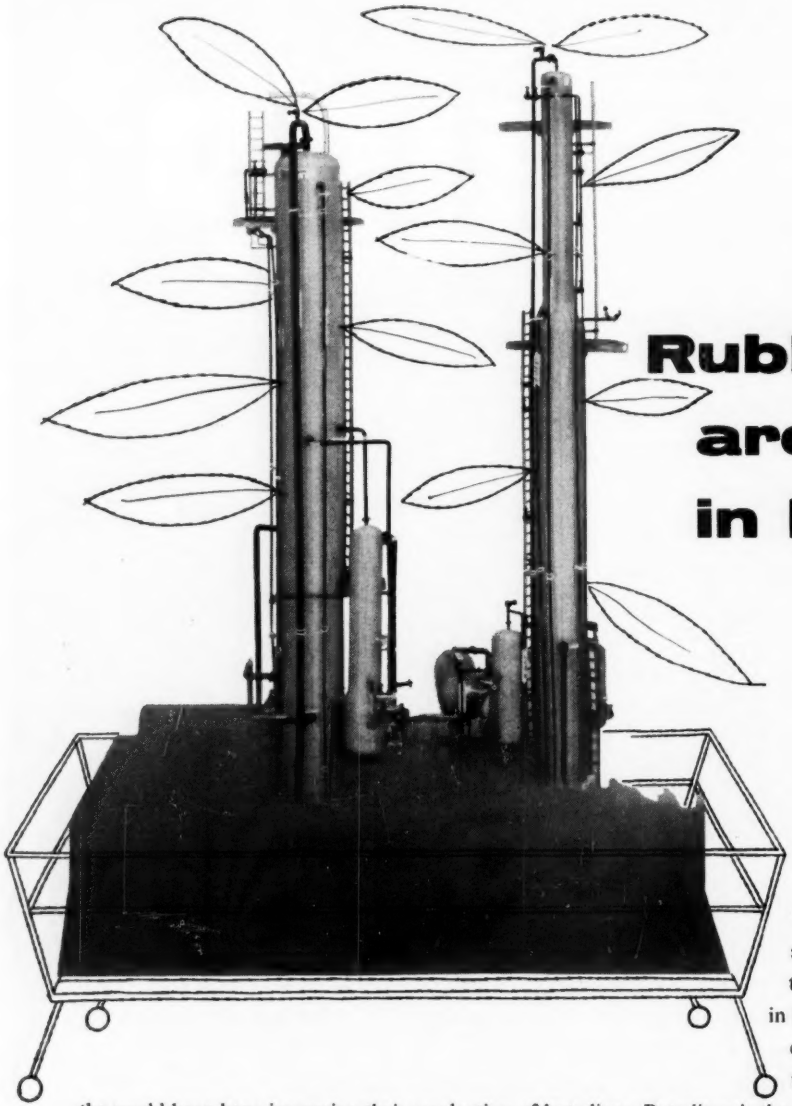

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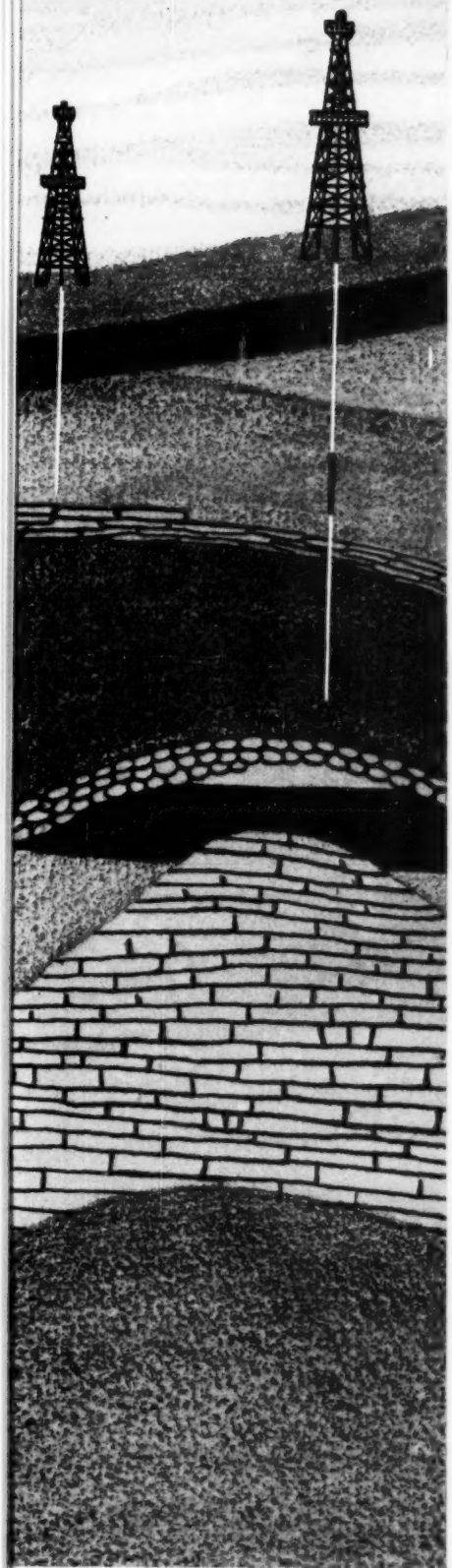

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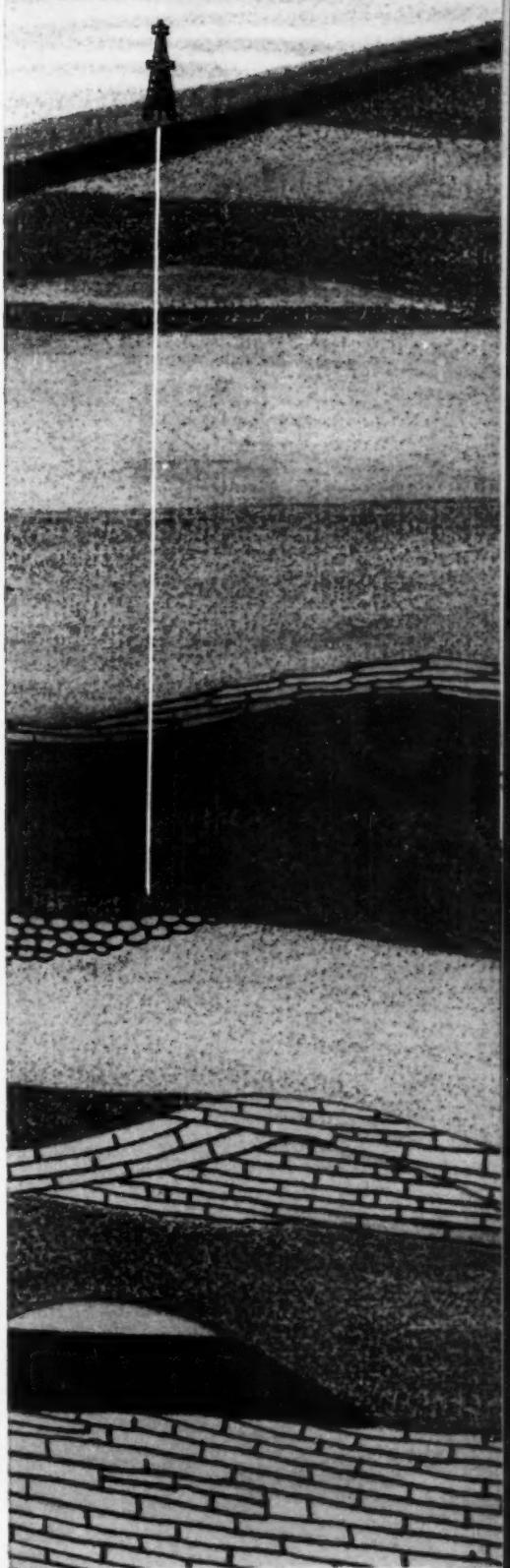

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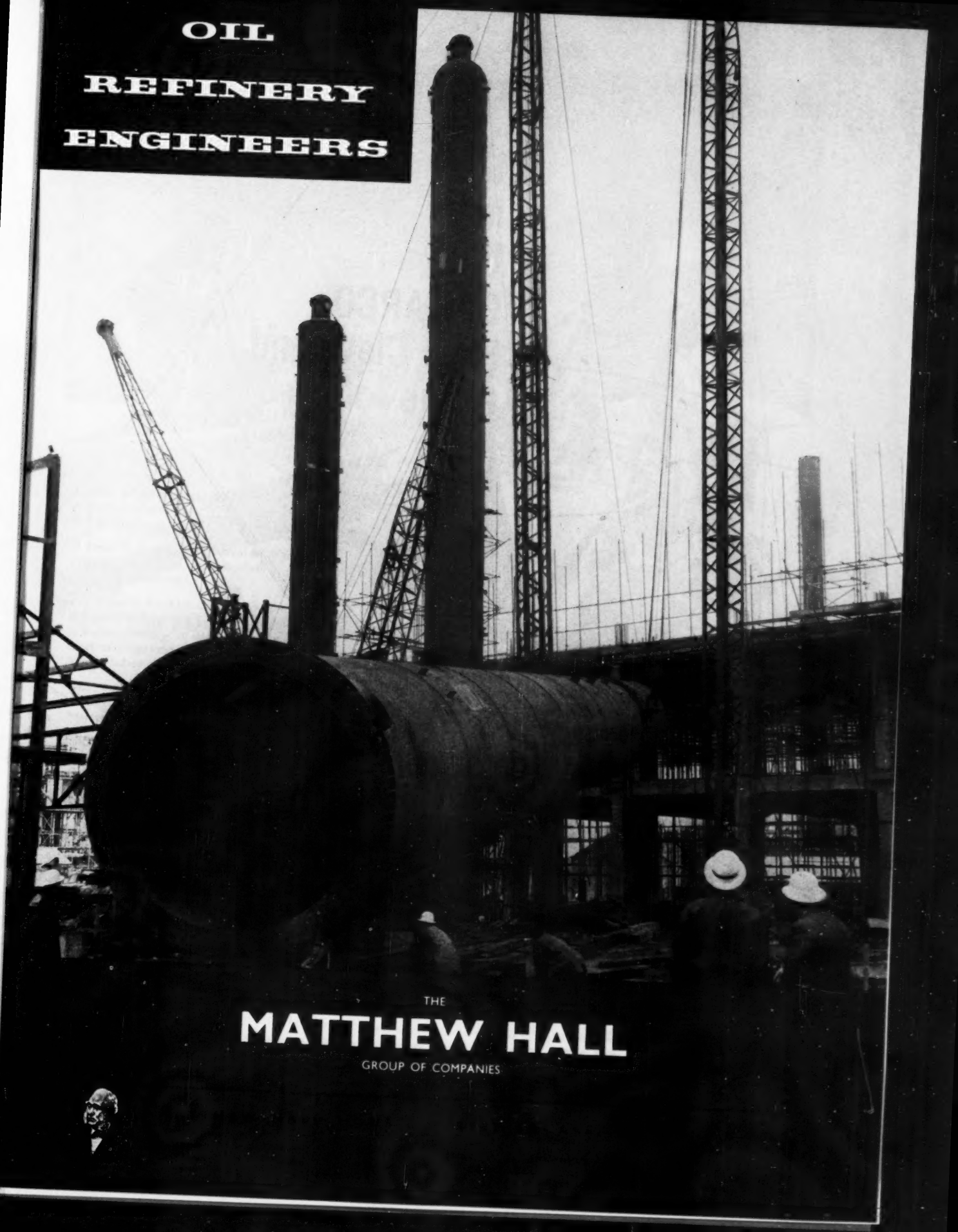
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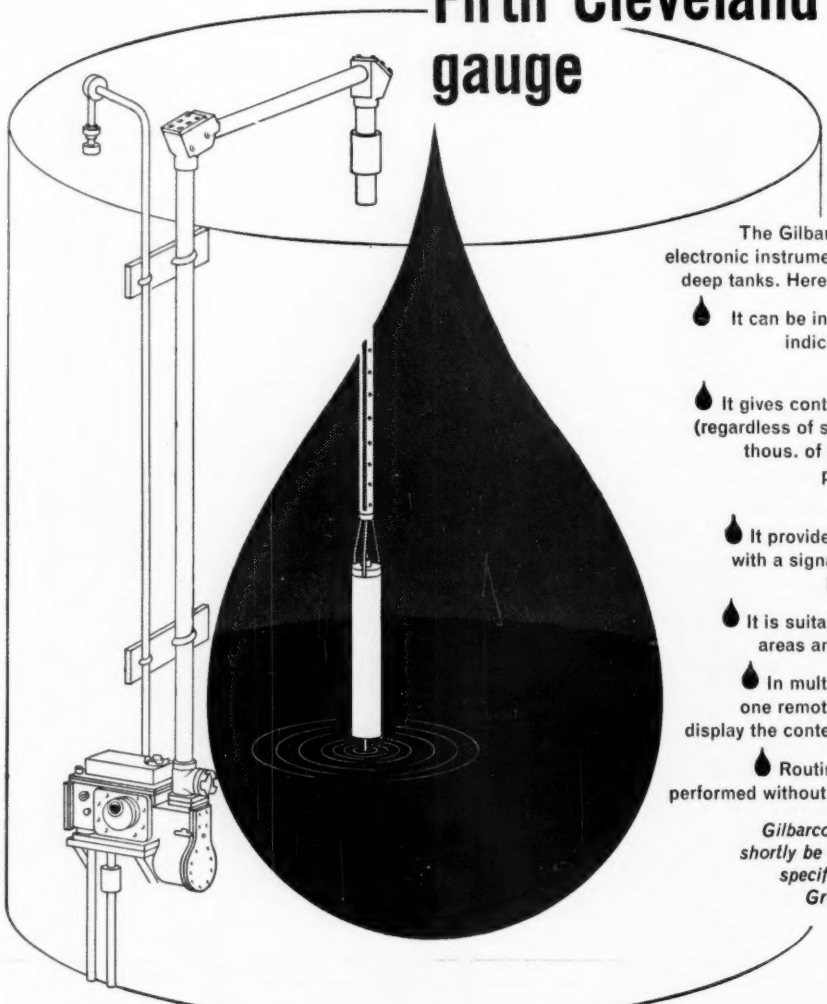

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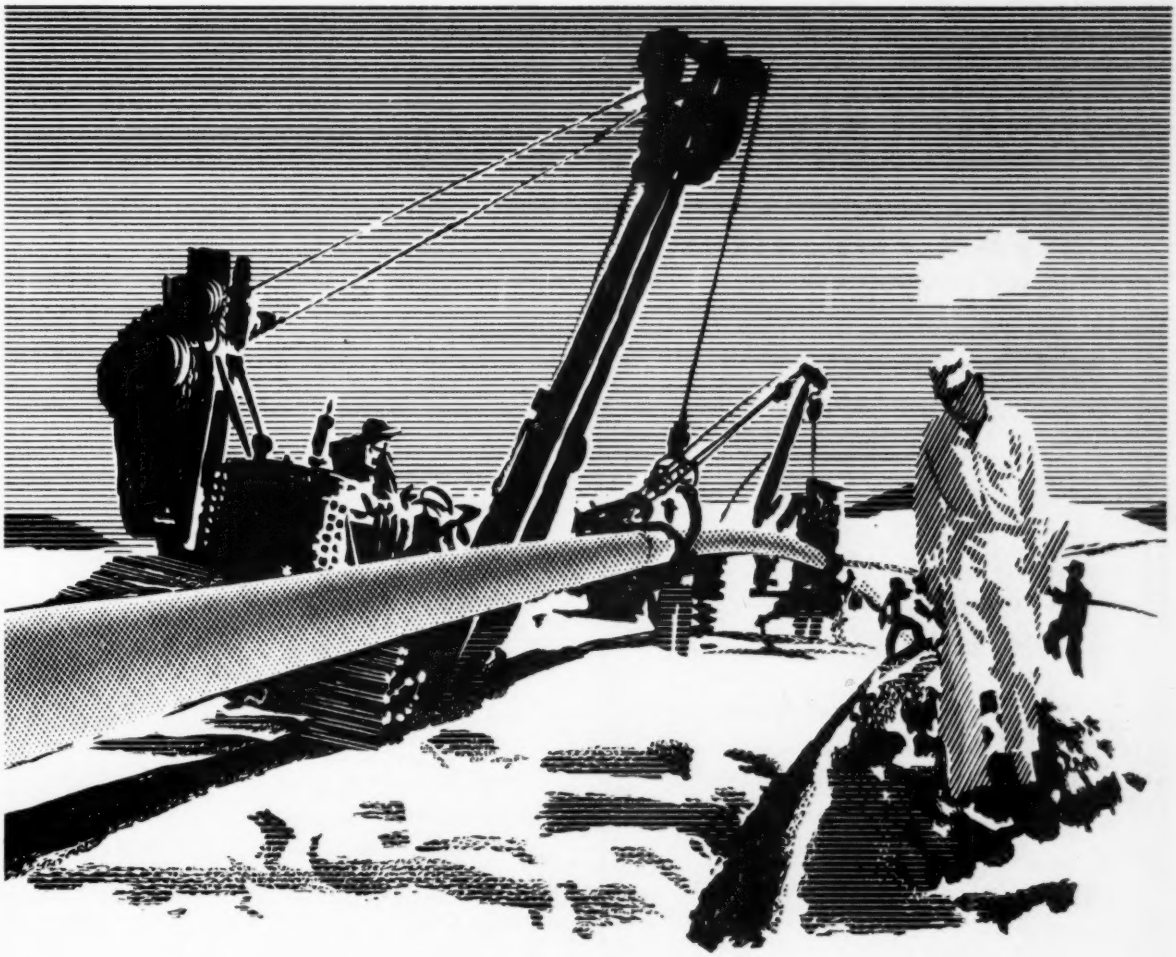

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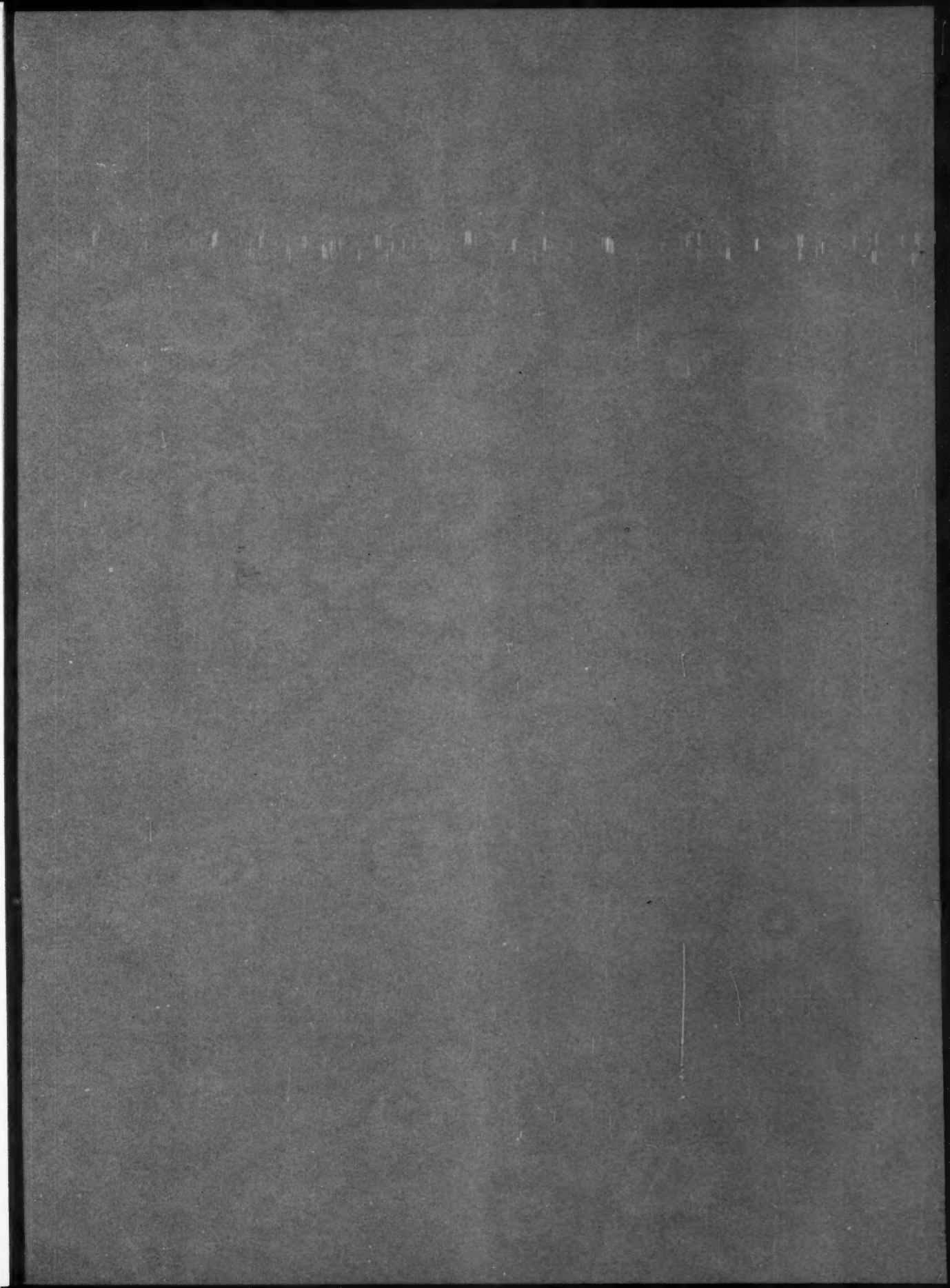

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